Review

A review of DNA functionalized/grafted carbon nanotubes and their characterization

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Abstract

The functionalized carbon nanotubes (CNTs) are believed to be very promising in the fields such as preparation of functional and composite materials and biological technologies. Immobilization of nanotubes with specific recognition biosystems indeed provides ideal miniaturized biosensor. A prerequisite for the search in this area is the development of chemical methods to immobilize biomolecules onto carbon nanotubes in a reliable manner. The DNA-based biomolecular recognition principle has been applied to CNTs to constant nanotube electronic devices as well as CNT–DNA electrochemical sensors. The sp^2 hybridization and the outstanding electronic properties of the nanotubes coupled with their specific recognition properties of the immobilized system indeed make CNTs, an ideal biosensor. DNA immobilization has been paid great attention and considered as a fundamental methodology for the construction of DNA biosensors. Successful integration of CNTs in electronic devices and sensors requires controlled deposition at well-defined locations and appropriate electrical contacts to metal leads. Different methods for achieving this goal are directional growth of the tubes, alignment by mechanical forces, alignment by electric and magnetic fields, patterned- and self-assembly.

Also the concept of using DNA to direct the assembly of nanotubes into nanoscale devices is attracting attention because of its potential to assemble a multicomponent system in one step by using different base sequence for each component. Thus, DNA functionalization of CNTs holds interesting prospects in various fields including solubilization in aqueous media, nucleic acid sensing, gene-therapy and controlled deposition on conducting or semiconducting substrates. This review highlights the functionalization/grafting of DNA onto single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) with or without self-assembly which can be employed in fabricating biosensors for selective recognition of DNA. The review also addresses various characterization techniques that have been employed by various researchers to give the readers an insight into the planning of experiments and subsequent interpretation.
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Contents

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1. Introduction

Carbon nanotubes (CNTs) are a new allotrope of carbon originated from fullerene family, which will revolutionize the future nanotechnological devices [1]. CNTs can be imagined as rolled up graphite sheets held together by van der Waal's bonds. These nanosized near perfect whiskers were first noticed and characterized in 1991 by Iijima [2] of NEC Corporation in Japan. CNTs are elongated fullerenes that can be produced with exactly 12 pentagons and millions of hexagons [3]. They have a long cylinder made of hexagonal honey comb of lattice of carbon, bound by two pieces of fullerenes at the ends. The first nanotubes observed were multiwalled CNTs (MWCNT) which consist of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow area with a spacing between the layers which is close to that of the interlayer separation as in graphite (0.34 nm) [4]. In contrast, single shell or single walled nanotubes [5,6] (SWCNT) are made of single grapheme (one layer of graphite) cylinders and have a very narrow size distribution(1–2 nm). Both types of nanotubes have the physical characteristics of solids and are microcrystals, although their diameters are close to molecular dimensions.

Carbon nanotubes have aroused increasing interests of many researchers due to their remarkable tensile strength, high resilence, flexibility and other unique structural, mechanical, brilliant electrical and physicochemical properties [7,8]. Carbon nanotubes (CNTs) can be either metallic or semiconductive depending on their helicity and diameter, i.e. depending on the atomic structure, the CNTs behave as a metal or semiconductor. The exciting electronic properties suggest that CNTs have the ability to promote the electron transfer reactions when used as an electrode in electrochemical reactions [9]. The electrical conductivity of CNTs can be altered by modifying the parent structure. Thus, a novel strategy of altering the electronic properties of nanotubes are done either by chemically functionalizing them with a moiety or altering the structure whose intrinsic properties are electrically configurable. By doping the CNT with nitrogen, the semiconducting nanotubes becomes metallic [10]. This change in electronic properties makes CNTs an ideally suited material for the inter-connects in nanoelectronic devices.

Also the electrical transport studies on CNTs reveal that they can behave as quantum wires at low temperature [11].

The nanodimension of the CNTs provide very large surface area. The surface area of the SWCNTs were found to be one magnitude higher than that of graphite but smaller compared to the activated porous carbon. Similarly, due to the relatively large hollow channels in the centre of nanotubes, their density is very low compared to graphite. Rough estimates suggest that SWCNT density could be as small as $0.6\,g/cm^3$ and MWCNT density could range from 1 to $2\,g/cm^3$ depending on the constitution of the samples. The porosity and the reactivity of the CNTs make them an ideal candidate for the storage of neutral species as well as electron donors [12]. Also since CNTs are having high surface area, they are better substrates than amorphous glassy carbon in studying the immobilization or growth of biomolecules [13]. The incorporation of superstrong light weight CNT structures into organic and inorganic polymeric matrices offers a novel approach to the design of high performance composite and ceramic materials with super mechanical properties [14,15].

Like graphite, CNTs were relatively non-reactive, except at the nanotube caps which are more reactive due to the presence of the dangling bonds. The reactivity of the sidewalls of the carbon nanotube π-system can be influenced by the tube curvature or chirality. Loung et al. [16] reported that when CNTs were sonicated in organic solvents, they produce dangling bonds that will undergo further chemical reactions. Due to the less solubility of CNTs in any of the solvents, it is also very difficult to isolate one carbon nanotube from the other. The organic functional groups chemically attached to the CNTs assist effectively in unroping the nanotube bundles and improving their solubility. The reactivity of CNTs depends on the curvature of their surface. This review highlights the functionalization/grafting of DNA onto SWCNTs and MWCNTs with or without self-assembly which can be employed in fabricating biosensors for selective recognition of DNA.

2. Chemical modification of CNTs

Experiments on opening multiwalled tubes with acids and other reagents could result in the formation of surface carboxy-

late and other groups on the nanotube surfaces. More recently attempts have been made to functionalize SWCNT. For example, in late 1998, a group from University of Kentucky [17] described a method for dissolving SWCNT in organic solutions by derivatization with thionyl chloride and octadecyl amine. This approach opened the way for solution phase chemistry to be carried out on SWCNTs. Immobilization of nanotubes with specific recognition biosystems indeed provide ideal miniaturized biosensor. A prerequisite for the search in this area is the development of chemical methods to immobilize biomolecules onto carbon nanotubes in a reliable manner.

DNA offers great potential as a building block with all the basic properties necessary for the assembly of nanoscale electronic devices with their potential applications in decentralized clinical testing, environmental monitoring and food safety. The construction of DNA electronic nanodevices is possible and will also be a predominant technique of new molectron with attendant benefits of miniaturization, low power requirements, high efficiency and low heat generation [9]. DNA immobilization has been paid great attention and considered as a fundamental methodology for the construction of DNA biosensors. The viability of DNA biosensors requires an intimate connection between the nucleic acid system and electronic transducer. Various methods of surface capturing of DNA include chemical adsorption, covalent binding, electrostatic attraction, copolymerization, and via the avidin–biotin affinity system [18]. It can be teethered to wider ranging substrates, can direct assembly with specificities that greatly exceed that of any specific molecule. It is relatively robust and can be synthesized with tags such as fluorescent molecules to enable rapid detection of bioevents. A few of the approaches that have been studied todate include the mineralization of DNA, the use of DNA to assemble nanotubes/nanoparticles and larger colloidal particles and in fabrication of biosensors. Thus, by chemically grafting single-stranded DNA (ssDNA) onto aligned carbon nanotube electrodes resulted in selective and sensitive recognition of complementary DNA. CNTs can amplify DNA or protein recognition and transduction events resulting in an electrical biosensing of DNA or proteins.

Successful integration of CNTs in electronic devices and sensors requires controlled deposition at well-defined locations and appropriate electrical contacts to metal leads. Different methods for achieving this goal were directional growth of the tubes, alignment by mechanical forces, alignment by electric and magnetic fields, patterned- and self-assembly [19]. Controlled self-assembly of CNTs was achieved by interphasing them with biological molecules including DNA. This approach has considerable potential for driving self-assembly of CNT-based devices in light of the intense richness of biological recognition.

3. CNTs as sensors

The unique structural, electrical and mechanical properties of CNTs make them extremely attractive for the task of electrochemical sensing. Electrodes modified with CNTs have been employed for the detection of important biomolecules including Cytochrome *c*, ascorbic acid, NADH, etc. [20]. A wide range of inorganic and biological molecules can be adsorbed onto nanotube in the hope of using them as highly accurate tiny sensors [10]. CNTs have been recently used as transducers for enhanced electrical detection of DNA hybridization [21]. The utility of CNTs in electrochemical biosensing schemes will definitely benefit from their charge transfer characteristics while approaching the size of the biomolecules. The sp^2 hybridization and the outstanding electronic properties of the nanotube coupled with their specific recognition properties of the immobilized system indeed make CNTs, an ideal biosensor. CNTs can be used for the sensing of gas molecules like O_2, NH_3, O_3, etc., since a characteristic change in electrical properties of the CNTs takes place on exposure of them with these gases [10]. CNTs can also be used for dramatically amplifying enzyme-based bioaffinity electrical sensing of proteins and DNA [22]. Male et al. [23] used the combination of nanoparticles and CNTs to modify glassy carbon or an electrode to improve the electroactivity and selectivity for glucose.

4. Functionalized/grafted CNTs

4.1. Functionalization/grafting of CNTs

The surface functionalization will aid the carbon nanotube materials in becoming biocompatible, improving their solubility in physiological solutions and selective binding to biotargets. The functionalized CNTs were believed to be very promising in the fields such as preparation of functional and composite materials and biological technologies [24].

The functionalization of CNTs may be separated into two categories—a noncovalent wrapping or adsorption and the covalent tethering. Strano [10] reported that there is no covalent interaction between the proteins and the nanotubes, thus describing the functionalization due to physisorption. The best stability, accessibility and selectivity will be achieved through covalent bonding because of its capability to control the location of the biomolecule, improved stability, accessibility, selectivity and reduced leaching [25]. The chemicals that can form covalent or irreversible van der Waal's bonds with the nanotube could alter the sp^2 hybridization of CNTs to sp^3 hybridization, as a result of functionalization.

In order to attach the molecules to the nanotubes covalently, the first requirement is the formation of functional groups on the CNTs. The carboxylic acid group is often the best choice because it can undergo a variety of reactions and is easily formed on CNTs via oxidizing treatment. Functionalized CNTs have received much interest for dispersion enhancement in processing or chemical modification. Shortening of CNTs by ultrasonication with oxidizing acid mixtures is frequently used to functionalize CNTs [26]. To introduce selectivity to nanotube-based sensors, certain functional groups that can selectively bind to specific target molecules need to be anchored on the nanotube surface. The sidewall of CNTs is chemically stable, making the functionalization of CNTs with sensing molecules, a challenge. Also the covalent modification of the nanotube sidewalls totally change the electronic properties of the CNTs. So, for the development of CNT-based sensors, noncovalent modification of the
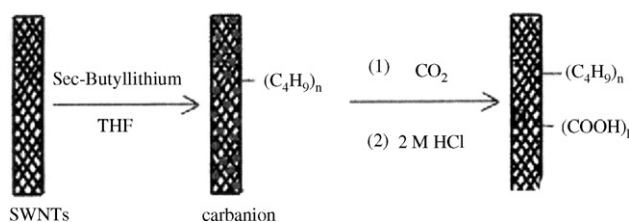
Fig. 1. Schematic representation of the carboxylation of CNTs [24].

sidewall of CNTs were found to be reliable. Xiao et al. recently [27] reviewed the progress in the functionalization of CNTs. Also the use of carbon nanotubes as an analytical tool in filters, membranes, sorbent material for solid phase extraction, in electrochemical sensors, and in separation methods were recently reviewed by Valcarcel et al. [28]. Kohli and Martin [29] describes that nanotubes have large inner volumes, which can be filled with any desired chemical or biochemical species ranging in size from proteins to small molecules. Also nanotubes have distinct inner and outer surfaces, which can be functionalized either chemically or biochemically. Thus, the development of simple and cost effective chemical methods for covalent functionalization of carbon nanotube materials is becoming an area of growing fundamental and industrial importance.

4.2. Techniques of functionalization of CNTs

Hu et al. [8] functionalized CNT with the molecules containing thiol group and halogen. The chemical methods for the covalent functionalization of CNTs involve direct fluorination, organic free radical addition, fluorine displacement in fluoro nanotubes producing amino, hydroxyl and carboxy group terminated derivatives. The carboxylation is conducted via oxidation of defect sites in CNTs by strong oxidants. The alkylation and acylation of CNTs can be realized by making use of fluorine displacement reactions of fluoronanotubes with alkyl lithium reagents or by employing diazonium chemistry for attaching acyl groups to the sidewalls [24]. By treating the CNT with secondary butyl lithium firstly and reacting the generated carbanions with carbon dioxide secondly, it can be alkylated and carboxylated and its schematic representation is given in Fig. 1. Huang et al. [13] attached the proteins to carbon nanotubes via the diimide activated amidation and is illustrated in Fig. 2. They also reported that the BSA conjugates thus obtained after attachment with CNTs are highly water-soluble, forming dark coloured aqueous solution.

Other functionalizations in CNTs include fluorination [30], 1,3-dipolar addition [31], derivatization of small diameter SWC-
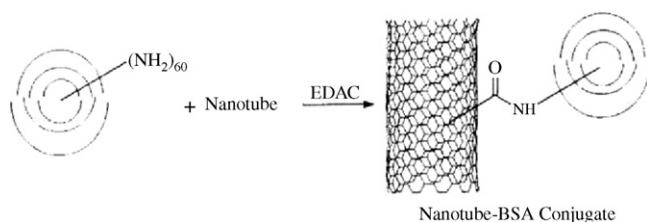

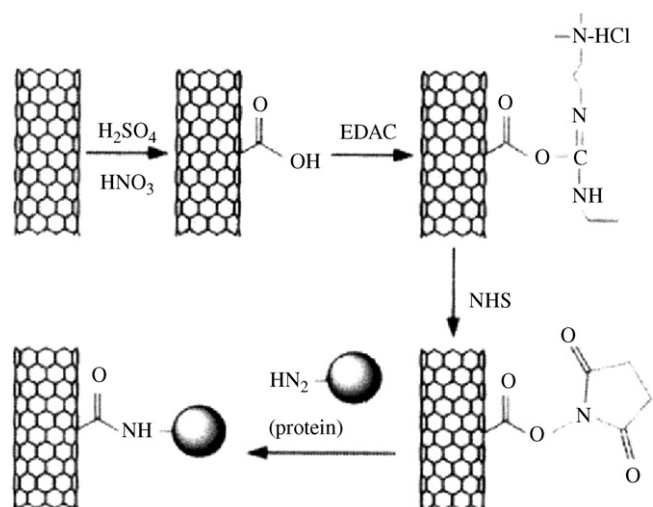Fig. 2. Functionalization of CNTs via diimide activated amidation [13].

Fig. 3. Schematic view of the attachment of proteins to CNTs via diimide activated amidation [25].

NTs [32], glucosamine attachment [33] and sidewall carboxylic functionalization of SWCNTs [34].

One of the universal methods for connecting biomolecules to CNTs is diimide activated amidation by direct coupling of carboxylic acid to proteins using N-ethyl-N-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDAC) or N,N'-dicyclohexyl carbodiimide (DCC) as a coupling agent [25]. The schematic view of the attachment of proteins to CNTs via diimide activated amidation is given in Fig. 3. Functionalization of CNTs were also carried out using 1-pyrenebutanoic acid [35], succinimidyl ester [36] for the immobilization of biomolecules, anti-fullerene IgG monoclonal antibody bound to SWCNTs [37]. Proteins and DNA have also been used to modify MWCNTs [38,39]. Fu et al. [40] reported the selective functionalization of SWCNT sidewalls with a thin layer of SiO_2 and that offer flexible ways for further modification utilizing the chemistry available for the silica surface. Ramanathan et al. [41] functionalized SWCNT with amino groups via chemical modification of carboxyl groups introduced on the carbon nanotube surface. The amino termination further allows the functionalized SWCNTs possible for covalent bonding to polymers and biological systems such as DNA and carbohydrates. The common outcome of these functionalization is the increased solubility of CNTs either in the organic solvent or water.

5. DNA functionalized/grafted CNTs

5.1. DNA-based sensors

DNA is an important and promising molecule with all the basic properties necessary for the assembly of nanoscale electronic devices. The combination of CNT with DNA has attracted the attention of several research groups recently. DNA chains have been used to create various functional structures and devices through the sequence-specific pairing interactions. The DNA-based biomolecular recognition principle has been applied to CNTs to construct nanotube electronic devices as well as

CNT–DNA electrochemical sensors. Guo et al. [9] described the electrochemical characteristics on the immobilization of both double-stranded and single stranded calf thymus DNA molecules on the surface of MWCNTs.

DNA functionalization of CNTs holds interesting prospects in various fields including solubilization in aqueous media, nucleic acid sensing, gene-therapy and controlled deposition on conducting or semiconducting substrates. DNA molecules can increase CNT solubility and also be used to distinguish metallic CNT from semiconducting CNTs. The DNA attachment occurs predominantly at or near the nanotube ends. The rare attachment of DNA to other regions of CNTs indicates that it is the result of sequence specific polynucleic acid–DNA base pairing rather than nonspecific interactions [42]. The individual CNTs can be functionalized with special selectivity and can be used to differentiate between the two DNA sequences. The concept of using DNA to direct the assembly of nanotubes into nanoscale devices is attracting attention because of its potential to assemble a multicomponent system in one step by using different, base sequence for each component. The reactive sites on the CNTs were created by the acid treatment to introduce the carboxyl groups on their tips. DNA molecules with functional linkers are then coupled to the carboxyl groups on the CNTs. Chen et al. [43] developed a multistep method to covalently functionalize multiwall carbon nanotubes with DNA and oligonucleotides. Thus, the bioconjugates of carbon nanomaterials and DNA will have potential uses in many areas due to the combination of unusual structure of carbon nanomaterials and bioactivity of DNA [44]. Hazani et al. [45] reported the confocal fluorescence imaging of SWCNT–DNA adducts obtained by carbodiimide-assisted coupling of amine functionalized oligonucleotides to oxidized SWCNTs. CNTs have been recently used as transducers for enhanced electrical detection of DNA hybridization [21]. The DNA sensing application require high sensitivity through amplified transduction of the oligonucleotide interaction. The wrapping of CNTs in DNA results in some interesting effects. The DNA nanotube species are highly soluble in water removing the requirement for surfactants. Also the negative charges on the phosphate group of DNA results in the charging of DNA nanotube species.

The bifunctional chemical structure of CNTs would facilitate the selective attachment of multiple DNA sequences using two distinct DNA–CNT linking strategies. In one strategy, by accessing the free carboxyl groups of CNTs, single stranded, amine terminated DNA oligonucleotides are attached to the CNT array using amide coupling chemistry in aqueous/organic solvent mixtures. The second strategy involves the attachment of oligonucleotides to the sidewalls of the CNTs through hydrophobic interactions. Taft et al. [46] reported the immobilization of DNA through the interaction of the hydrophobic pyrene group with the graphite-based sidewalls of the CNTs, which was highly specific and DNA-dependent process.

The unique property of the specific molecular recognition of DNA coupling with SWCNTs and hybridizing these macromolecular wires will provide a versatile means of incorporating SWCNTs into larger electronic devices by recognition-based assembly and using SWCNTs as probes in biological systems
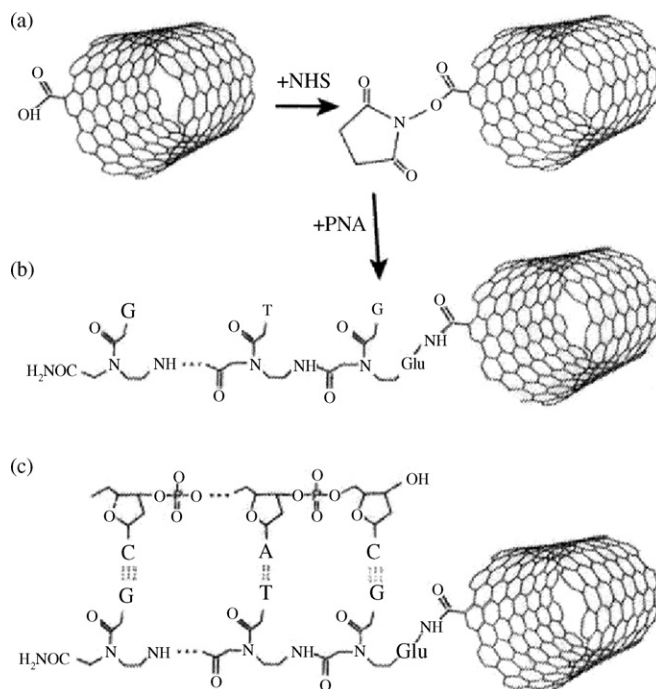

Fig. 4. Attachment of DNA to CNTs. (a and b) *N*-Hydroxysuccinimide esters formed on carboxylated SWNT are displaced by peptide nucleic acid forming an amide linkage. (c) DNA fragment with a single-stranded sticky end hybridizes by Watson–Crick base-pairing to the PNA-SWNT [42].

by sequence-specific attachment [42]. Fig. 4 shows the different modes of attachment of DNA to CNTs. Buzaneva et al. [47] developed the nanotechnology for the formation of the multifunctional CNT cells using theoretical predictions. The most ideal approach for DNA immobilization in CNTs is covalent binding on a solid surface via a single point attachment. Most of the applications of immobilized oligonucleotide are based on the hybridization between immobilized oligonucleotide and its complementary DNA sequence in the sample [48].

Wang et al. [20] reported that the strong accumulation of phenolic products of alkaline phosphatase onto CNT-modified electrodes allow the detection of extremely low levels of the target DNA. Enhanced voltammetric response of phenolic compounds at CNT modified glassy carbon electrodes was measured in connection with enzyme-based electrochemical detection of DNA hybridization.

The detailed mechanism behind the dissolution of nanotubes in DNA is not clear at present. Nakashima et al. [49] suggested that the π–π interactions between the nanotube sidewalls and the nucleic acid bases may be responsible. There may also be some weak interaction between the major and minor grooves of the DNA and the nanotubes.

Cai et al. [18] reported the application of CNTs to the fabrication of an electrochemical DNA biosensor for the specific DNA sequence detection. Fig. 5 shows the schematic representation of the enhanced electrochemical detection of DNA hybridization based on the MWCNTs-COOH constructed biosensor. Moghaddam et al. [50] firstly reported the azide photolysis for the functionalization of CNTs and the scheme used for the function-
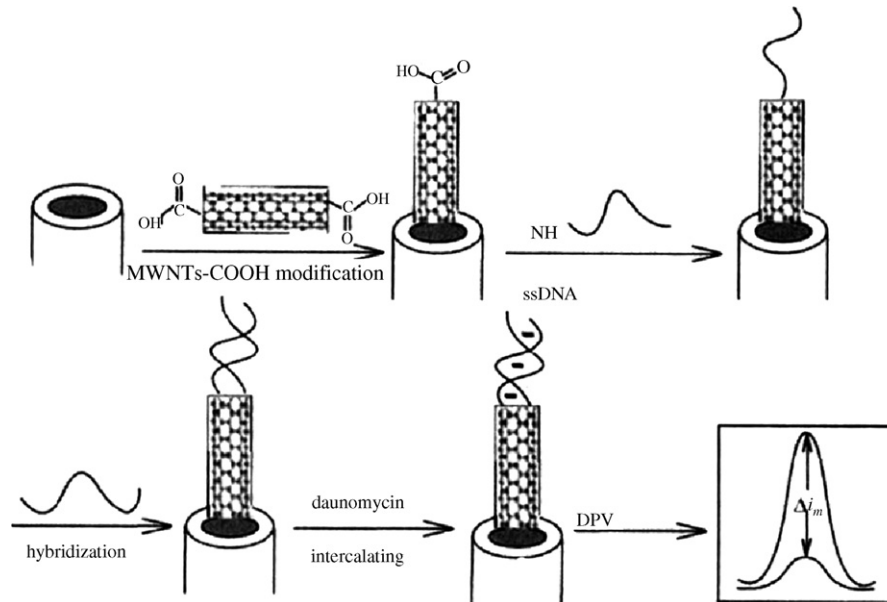
Fig. 5. Schematic representation of enhanced electrochemical detection of DNA hybridization based on the MWNTs-COOH constructed DNA biosensor [18].

alization is given in Fig. 6. He used the azide-photochemistry to functionalize the sidewalls and tips of CNTs in a solid-state reaction and the subsequent synthesis of a DNA oligonucleotide from the reactive group on each photoadduct.

Lu et al. [51] investigated a system consisting of B-DNA and an array of carbon nanotubes periodically arranged to fit into major grooves of the DNA. They discussed in detail about the system used as an electronic switch or as a sensor device for ultra fast DNA sequencing. A novel sensitive electrochemical biosensor based on magnetite nanoparticle for monitoring DNA hybridization by using MWCNT – COOH/ppy – modified glassy carbon electrode was described by Cheng et al. [52].

CNTs can amplify DNA, protein recognition and transduction events. This property were used for the ultrasensitive method for the electrical biosensing of DNA or proteins. An effective DNA sensing system to detect specific nucleic acid sequences is playing an important role in many areas such as clinical diagnosis, medicine, epidermic prevention, environmental protection and bioengineering.

5.2. DNA directed self-assembly

The delivery of gold nanoparticles to CNTs using the self-assembly properties of DNA represents an advance towards
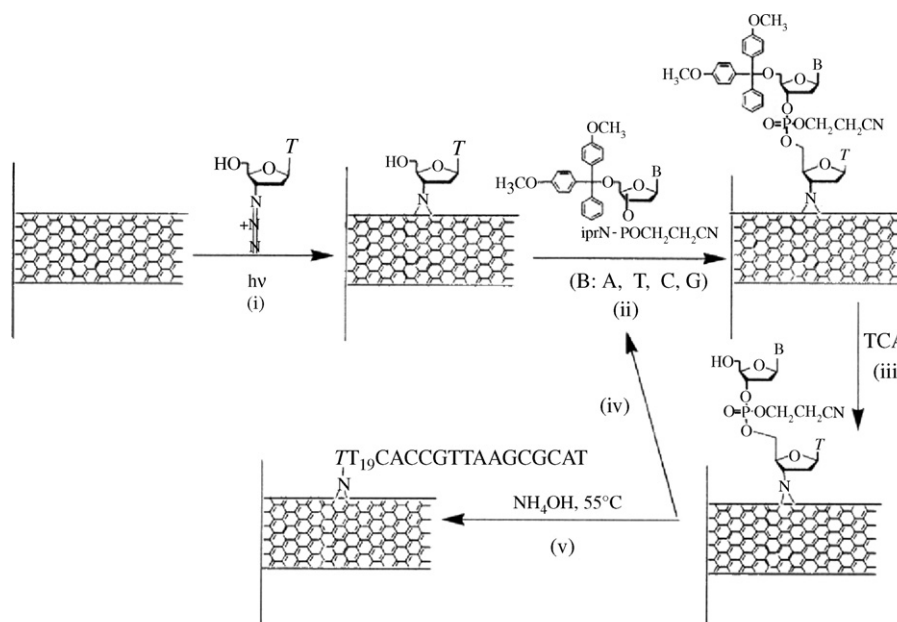

Fig. 6. Azide photolysis of CNTs [50].

building higher order nanostructures with rational control. The controlled self-assembly of CNTs was recently achieved by interphasing the CNTs with biomolecules. This approach has considerable potential for driving self-assembly of CNT-based devices in the light of the immense richness of biological recognition. The approach involves two steps. In the first step, a self-assembled nanolayer of single stranded DNA is adsorbed onto Au contacts by reaction with thiol terminated oligonucleotides and in the next step, the oxidized CNTs modified with oligonucleotides of the complementary sequence are allowed to hybridize with the DNA located on the Au contacts. Hazani et al. [19] used a long DNA molecule featuring Rec A proteins as a scaffold, onto which streptavidin-functionalized SWCNTs were assembled utilizing anti-ReeA primary antibodies and biotinylated secondary antibodies. Wang et al. [53] reported a novel DNA immobilization strategy, in which the DNA probes are adsorbed on self-assembled multiwalled nanotubes. Their results showed that this immobilization strategy based on self-assembled MWCNTs yields a higher hybridization efficiency than that adsorbed on random MWCNTs. Li et al. [54] demonstrated that a wide range of multicomponent structures of CNTs can be constructed by DNA directed self-assembling of CNTs and gold nanoparticles.

Banerjee and Wong [55] reported that by varying the nature of the organic capping groups on the nanocrystal surface and the organic bifunctional linkers, it is possible to modulate interactions between the nanotubes and the nanocrystals with implications for self-assembly. Wang et al. [53] developed DNA biosensors based on the self-assembly of carbon nanotubes. They assayed the hybridization by the changes in the voltammetric peak of the indicator methylene blue and the results showed that the DNA biosensors based on the self-assembled MWCNTs have a higher hybridization efficiency than that based on random MWCNTs. Fig. 7 shows the schematic representation procedure for DNA directed self-assembly of multiple CNT and nanoparticles.

Thus, the use of carbon nanotubes as building blocks in the nano/microelectronic device could revolutionize the electronic industry in the same way that the microchips have revolutionized the computer industry.

6. Characterization of functionalized CNTs

Belin and Epron [56] have recently reviewed various characterization methods for CNTs. As pointed out by these authors, a limited number of techniques are available for the investigation of the morphological and structural characterization of CNTs. Of these, scanning tunneling microscopy and transmission electron microscopy are only useful in characterizing CNTs at the individual level. X-ray photoelectron spectroscopy (XPS) is helpful in determining chemical structure of nanotubes, while neutron and X-ray diffraction, infra red and Raman spectroscopy are mostly used in global characterization techniques.

6.1. UV–vis–near IR spectrometry

Hazani et al. [45] have recorded the UV–vis spectra of the soluble fractions obtained from the coupling steps with oligonucleotides 5′CTA-AGA-TTT-TCT-GCA-CATTAT-TG3′-aminoheptyl (C_1) and 5′CTA-AGA-TTT-GCA-TAG-TCT-GCA-TAG-GAT-TAA-TG3′ (C_2). The UV–vis spectra of these two conjugates clearly indicate that much more DNA is present in the soluble fraction resulting from the coupling with C_1. Also the visual appearance and the UV–vis spectra of the different samples indicate that majority of the DNA present in the adduct was covalently bounded rather than simply physisorbed. On the other hand, the functionalization of SWCNTs with enzymes results in the featureless UV–vis spectra taken in weak aqueous solutions [57]. This observation is similar to the studies by Huang et al. [13]. The featureless spectra in the UV–vis region indicate the disruption in the one-dimensional electronic structure of the SWCNTs due to the bond formation as
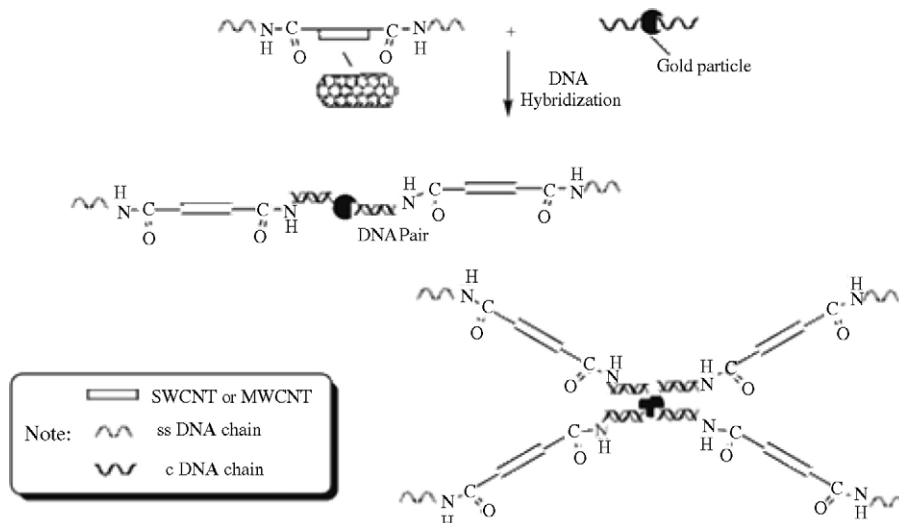

Fig. 7. Schematic representation of procedure for DNA directed self-assembling of multiple CNTs and nanoparticle [54].

a result of functionalization [58–61]. Hu et al. [8] functionalized the CNTs with molecules containing thiol groups and halogen. They also reported a typical featureless spectrum in the UV–vis region for the HS-CNTs. The UV–vis spectrum of SWCNTs reacted with CdSe nanocrystals, capped with mercaptothiol in methanol showed a small blue shift upon capping with thiol in the ligand exchange reaction and the peaks of the optical features were also somewhat broadened with samples capped with the aliphatic mercapto derivatives [62].

Buzaneva et al. [47] also characterized the DNA layer on KRS-5 substrate deposited from DNA/NaOH/carbon nanotube and DNA–NaOH by taking their absorption spectra and found that (i) the maximal absorption changes from 285.4 nm (DNA layer) to 279.3 nm (DNA–carbon nanotubes), (ii) the maximum widened for DNA–SWCNT layer, and (iii) the growing absorption range of 250–285.4 nm for DNA layer has broadened to 210–279.3 nm for DNA–SWCNT layer. The shift of absorption peak by 5.8 nm and its widening in case of DNA–SWCNT testify about the breaking of bonds between guanine-adenine and thymino-thytozyne in DNA molecule resulting in transformation of double spiral to chaotic ball.

6.2. Fluorescence imaging

DNA-functionalized carbon nanotubes were characterized by confocal fluorescence imaging by Hazani et al. [45]. The SWCNT–DNA adducts hybridize efficiently with the complementary strands with minimal nonspecific interactions with the noncomplementary sequences. This observation supports the notion that majority of DNA present on the SWCNT-C_1 conjugate is covalently attached rather than physisorbed to the nanotubes. Also the homogenous dispersions as well as the observation of distinguishable microscale features is a direct consequence of the aqueous solubility of the DNA functionalized SWCNTs.

6.3. FT-IR

Wang et al. [53] reported the FT-IR spectra of MWCNTs after functionalizing in HNO_3 solution. The peaks at 1742 and 3000 cm^{-1} corresponds to the $>$C=O and –OH stretch bands of the carboxylic groups. This reveals that carboxylic acid groups were introduced on the surface of the nanotubes. The DNA oligonucleotides linked with the nanotubes were also confirmed by the weak peak at 1715 cm^{-1} corresponding to the amide band.

The FT-IR spectra of purified CNTs showed a peak at 1711 cm^{-1} [12], which indicates the existence of the carboxylic acid groups. The peak centered at 1580 and 1174 cm^{-1} were assigned to be the C=C stretch of the CNT backbones and the C=O stretch of the acid group, respectively. They also reported that the peak of C=O shifts to 1733 cm^{-1}, as a result of functionalization and that frequency corresponds to the carboxylate ester. In the case of CNTs with amide linkages, a sharp peak in the region 1638 cm^{-1} [55] was observed. Wang et al. [57] reported the ATR-FT-IR spectrum of functionalized CNTs which shows a clear and sharp peak at 1710 cm^{-1}, corresponding to the C=O stretching vibration of the COCl group and the broad peak at

1530 cm^{-1} due to the stretching of the nanotube C=C bond located near to the COCl group. Also the C=O stretching frequencies of the amide bond formed by the functionalization appear at 1650 and 1640 cm^{-1}, respectively. As a result of DNA attachment with the functionalized CNTs, the intensity of the vibration mode at 1660 cm^{-1} (the vibration of C=O group) changed from 10% in DNA layer to 1.2% in DNA/SWCNT layer in the IR transmittance spectra [47].

6.4. Surface enhanced IR absorption (SEIRA)

Dovbeshko et al. [61] used SEIRA as a newer characterization technique for the study of the interaction of DNA with the SWCNT. In the case of DNA–SWCNTs, the changes in the vibrational modes of DNA were obtained and are the marker bands of the conformational state of DNA. The changes in the DNA marker bands shift of phosphate I band in high frequency region and low frequency shift in phosphate II band indicate the strong DNA interaction with SWCNT [61]. The spectrum also showed some transformation of H-bonds in the region of –OH, –NH and –CH vibrations as a result of DNA attachment with the SWCNTs. Furthermore, the DNA interaction with SWCNT leads to integral intensity increase of the vibrations in 600–900 cm^{-1} region. This evidence led to an assumption by authors that DNA interaction with SWCNT is based on wrapping of nucleic acid molecule around nanotube. However, this has to be confirmed by other experimental methods such as TEM.

6.5. Raman spectra

The Raman spectra of SWCNT show a very strong peak at 1593 cm^{-1} with a shoulder at 1571 cm^{-1} and low frequency mode at 162 cm^{-1} with shoulder at 148 and 177 cm^{-1} [60]. Also, the SWCNT Raman bands of are homogenously broadened due to the tube diameter distribution. Wang et al. [57] characterized the CNTs functionalized with amines and enzymes by Raman spectral studies.

6.6. Transmission electron microscopy (TEM)

The selective attachment of gold nanoparticles to the nitrogen doped carbon nanotubes were characterized by TEM [62]. The results showed that well-dispersed gold nanoparticles decorate the walls and ends of the nanotubes quite uniformly. The characterization of carbon nanotube–nanocrystal heterostructures reveals that the nanocrystals are linked to the oxidized CNTs, forming discrete nanocomposites and these nanocrystals tend to be concentrated at the open caps and the ends where there is the largest concentration of carboxylic groups and thus having the highest probability of amide bond formation [55]. The TEM images of functionalized carbon nanotubes with thiol groups and further attachment with Au nanoparticles show the self-assembly of Au nanoparticles on the functionalized CNTs. The Au nanoparticles with the even size of about 5 nm were dispersed into the HS-CNTs. The high resolution TEM images of functionalized multiwall carbon nanotube/gold nanoparticle

composites show that the typical length of functionalized MWC-NTs was about a few hundred nanometer and the typical diameter of MWCNTs ranged from 10 to 20 nm [63].

6.7. Atomic force microscopy (AFM)

Buzaneva et al. [47] characterized the DNA attached CNTs using AFM and the AFM image of the DNA layer showed regions with height up to 25 and 50 nm concerned to the different diffusion by water. The networks with pronounced structures were supposed to be the wrapped DNA. The AFM images for the SS DNA–SWCNTs, SS DNA–MWCNTs and complementary-DNA-Au nanoparticles indicated that no self-aggregation was caused by the attachment of DNA chains [54].

6.8. Scanning electron microscopy (SEM)

Wang et al. [57] reported the changes in the morphology of the functionalized carbon nanotubes using field emission scanning electron microscopy (FE SEM). After functionalization, the created defects and covalently attached amines cause the electrical conductivity of the CNT bundles to be decreased and results in partially blurred images of the functionalized SWCNTs with a reduction in the contrast and resolution. The SEM images of the amino-terminated SWCNTs incorporated epoxy polymer matrices indicate that the nanotube bundles were broken rather than just pull out at the surface, suggesting that covalent bonding exists between the epoxy matrix and SWNTs [7]. The oxidation of CNTs were also confirmed using SEM analysis by Banerjee and Wong [55].

6.9. X-ray photoelectron spectroscopy (X-PS)

Chemically functionalized MWCNTs and SWCNTs were characterized by Okapalugo et al. [1] by using high resolution XPS. These authors observed a significant chemical shift when the functional groups are covalently bonded to CNTs. Again, the attachment of –SH groups on the CNTs were also confirmed by XPS [8].

6.10. Electrochemical characterizations

Kerman et al. [64] characterized the multiwalled electrodes by voltammetric signals and they found that the signals obtained from modified electrodes were about 10-fold higher than that of the free MWCNTs. Also the sidewall functionalization of MWCNT enhanced the voltammetric response by about two-fold in comparison with the only end-oxidized MWCNT indicating the attachment of more amount of probes onto the surface.

The electrochemical characteristics on the immobilization of both double-stranded and single stranded calf thymus DNA molecules on the surface of MWCNTs have been investigated by cyclic voltammetry and electrochemical impedance analysis by Guo et al. [65]. As the immobilization time increases, the redox peak currents decrease rapidly. The results also reveal that most of the calf thymus DNA are covalently immobilized on the MWCNT via diimide activated amidation between the

carboxylic acid groups on the carbon nanotubes and the amino group on the DNA bases.

7. Summary

Ajayan [4] has vividly described the origin, development, distinguishing properties and futuristic scope of CNTs market place. The author has concluded that nanotubes as quantum wires in electronic devices is a promising field but most imminent applications are based on a combination of nanotubes and other materials such as filled polymer. The present review starts off with introduction giving concise account of CNTs and the use of carbon nanotubes as sensors followed by detailed account on need and subsequent virtues on functionalization/grafting of CNTs with various species. Furthermore, various reports that appeared in literature regarding the functionalization of CNTs in general and DNA grafted/functionalized CNTs in particular were critically discussed. The final section of the review concerns with various characterization techniques that have been employed by various researchers to give the readers an insight into the planning of experiments and subsequent interpretation. We sincerely hope the review kindles the interest in professionals in the field as well as in the beginners the exciting avenues that are in store in unraveling the truths of nature as well as commercial devices to be developed based on functionalized/grafted CNTs.

References

[1] T.I.T. Okapalugo, P. Papakonstaninuo, H. Murphy, J. McLaughlin, N.M.D. Brown, High resolution XPS characterization of chemical functionalized MWCNTs and SWCNTs, Carbon 43 (2005) 153–161.

[2] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56.

[3] T.W. Ebbesen, Carbon Nanotubes: Preparation and Properties, CRC Press, Boca Raton, FL, 1997.

[4] P.M. Ajayan, Nanotubes from carbon, Chem. Rev. 99 (1999) 1787–1799.

[5] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, Nature 363 (1993) 603–604.

[6] D.S. Bethune, C.H. Kiang, M.S. deVires, G. Gorman, R. Savoy, J. Vanquez, R. Beyers, Cobalt-catalysed growth of carbon nanotubes with single atomic-layer walls, Nature 363 (1993) 605.

[7] V.N. Khabashesku, J.L. Margrave, E.V. Barrera, Functionalized carbon nanotubes and nanodiamonds for engineering and biomedical applications, Diamond Relat. Mater. 14 (2005) 859–866.

[8] J. Hu, J. Shi, S. Li, Y. Quin, Z. Guo, Y. Song, D. Zhu, Efficient method to functionalize carbon nanotubes with thiol groups and fabricate gold nanocomposites, Chem. Phys. Lett. 401 (2005) 352–356.

[9] M. Guo, J. Chen, D. Liu, L. Nie, S. Yao, Electrochemical characteristics of the immobilization of calf thymus DNA molecules on multi-walled carbon nanotubes, Bioelectrochemistry 62 (2004) 29–35.

[10] M.S. Strano, Electronic structure control of single walled carbon nanotube functionalization, in: Proceedings of the Fifth International Conference on the Science and Application of Nanotubes, SanLuis Potosi, 2004.

[11] M. Burghard, G. Duesberg, G. Philipp, J. Muster, S. Roth, Controlled adsorption of carbon nanotubes on chemically modified electrode arrays, Adv. Mater. 10 (1998) 584–588.

[12] H.Z. Geng, X.B. Zhang, S.H. Mao, A. Kleinhammes, H. Shimoda, Y. Wu, O. Zhou, Opening and closing of single-wall carbon nanotubes, Chem. Phys. Lett. 399 (2004) 109–113.

[13] W. Huang, S. Taylor, K. Fu, Y. Lin, D. Zhang, T.W. Hanks, A.M. Rao, Y. Sun, Attaching proteins to carbon nanotubes via diimide-activated amidation, Nano Lett. 2 (2002) 311–314.

[14] P. Calvert, Nanotube composites: a recipe for strength, Nature 399 (1999) 210–211.

[15] E.T. Thostenson, Z.F. Ren, T.W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Comp. Sci. Technol. 61 (2001) 1899–1912.

[16] J.H.T. Loung, S. Hrapovic, D. Wang, F. Bensehaa, B. Simard, Solubilization of multiwall carbon nanotubes by 3-aminopropyltriethoxysilane towards the fabrication of electrochemical biosensors with promoted electron transfer, Electroanalysis 16 (2004) 132–139.

[17] K. Tanaka, T. Yamaba, K. Fukui, The Science and Technology of Carbon Nanotubes, Elsevier, New York, 1992, p. 267.

[18] H. Cai, X. Cao, Y. Jiang, P. He, Y. Fang, Carbon nanotube-enhanced electrochemical DNA biosensor for DNA hybridization detection, Anal. Bioanal. Chem. 375 (2003) 287–293.

[19] M. Hazani, F. Hennrich, M. Kappes, R. Naaman, D. Peled, V. Sidorov, D. Shvarts, DNA-mediated self-assembly of carbon nanotube-based electronic devices, Chem. Phys. Lett. 391 (2004) 389–392.

[20] J. Wang, A. Kawde, M.R. Jan, Carbon-nanotube-modified electrodes for amplified enzyme-based electrical detection of DNA hybridization, Biosens. Bioelectr. 20 (2004) 995–1000.

[21] J. Wang, G. Liu, M.R. Jan, Q. Zhu, Electrochemical detection of DNA hybridization based on carbon-nanotubes loaded with CdS tags, Electrochem. Commun. 5 (2003) 1000–1004.

[22] J. Wang, G. Liu, M.R. Jan, Ultrasensitive electrical biosensing of proteins and DNA: carbon-nanotube derived amplification of the recognition and transduction events, J. Am. Chem. Soc. 126 (2004) 3010–3011.

[23] K.B. Male, S. Harpovic, Y. Liu, D. Wang, J.H.T. Luong, Electrochemical detection of carbohydrates using copper nanoparticles and carbon nanotubes, Anal. Chim. Acta 516 (2004) 35–41.

[24] S. Chen, W. Shen, G. Wu, D. Chen, M. Jiang, A new approach to the functionalization of single-walled carbon nanotubes with both alkyl and carboxyl groups, Chem. Phys. Lett. 402 (2005) 312–317.

[25] K. Jiang, L.S. Schadler, R.W. Siegel, X. Zhang, H. Zhang, M. Terrones, Protein immobilization on carbon nanotubes via a two-step process of diimide-activated amidation, J. Mater. Chem. 14 (2004) 37–39.

[26] J. Liu, A.G. Rinzler, J. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Inverson, K. Shelimov, C.B. Huffman, F. Rodriguez Maeias, Y.S. Shon, T.R. Lee, D.T. Colbert, R.E. Smalley, Fullerene pipes, Science 280 (1995) 1253–1256.

[27] S.F. Xiao, Z.H. Wang, G.A. Luo, The progress in functionalization of carbon nanotube, Chin. J. Anal. Chem. 3 (2005) 261–266.

[28] M. Valcarcel, B.M. Simonet, S. Cardenas, B. Suarez, Present and future applications of carbon nanotubes to analytical science, Anal. Bioanal. Chem. 38 (2005) 1783–1790.

[29] P. Kohli, C.R. Martin, Template-synthesized nanotubes for biotechnology and biomedical applications, J. Drug Delivery Sci. Technol. 5 (2005) 49–57.

[30] E.T. Michelson, I.W. Chiang, J.L. Zimmerman, P.J. Boul, J. Lozano, J. Liu, R.E. Smalley, R.H. Hauge, J.L. Margrave, Solvation of fluorinated single-wall carbon nanotubes in alcohol solvents, J. Phys. Chem. B 103 (1999) 4318–4322.

[31] J. Chen, A.M. Rao, S. Lyuksyutov, M.E. Itkis, M.A. Haman, H. Hu, R.W. Cohn, P.C. Eklund, D.T. Colbert, R.E. Smalley, R.C. Haddon, Dissolution of full length single walled carbon nanotubes, J. Phys. Chem. B 105 (2001) 2525–2528.

[32] V. Georgakilas, K. Kordatos, M. Prato, D.M. Guld, M. Holzinger, A. Hirsh, Solvation of fluorinated single-wall carbon nanotubes in alcohol solvents, J. Am. Chem. Soc. 124 (2002) 760–761.

[33] J.L. Baher, J. Yang, D.V. Kosynkin, M.J. Bronikowski, R.E. Smalley, J.M. Tour, Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: a bucky paper electrode, J. Am. Chem. Soc. 123 (2001) 6536–6542.

[34] F. Pompeo, D.E. Resasco, Water solubilization of single-walled carbon nanotubes by functionalization with glucosamine, Nano Lett. 2 (2002) 369–373.

[35] P.G. Collins, K. Bradley, M. Ishigam, A. Zeltl, Extreme oxygen sensitivity of electronic properties of carbon nanotubes, Science 287 (2000) 1801–1804.

[36] R.J. Chen, Y.G. Zhan, D.W. Wang, H.J. Dai, Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization, J. Am. Chem. Soc. 123 (2001) 3838–3839.

[37] B.F. Erlanger, B.X. Chen, M. Zhu, L. Brus, Binding of an anti-fullerene IgG monoclonal antibody to single wall carbon nanotubes, Nano Lett. 1 (2001) 465–467.

[38] S.C. Tsang, Z.G. Guo, Y.K. Chen, M.L.H. Green, H.A.O. Hill, T.W. Hambley, P.J. Saddler, Immobilization of platinated and iodinated oligonucleotides on carbon nanotubes, Angew. Chem. Int. Ed. 36 (1997) 2198–2200.

[39] F. Balvonine, P. Schultz, C. Richard, V. Mallaoub, T.W. Ebbesen, C. Mioskowski, Helical crystallization of proteins on carbon nanotubes: a first step towards the development of new biosensors, Angew. Chem. Int. Ed. 38 (1999) 1912–1915.

[40] Q. Fu, C. Lu, J. Liu, Selective coating of single wall carbon nanotubes with thin SiO$_2$ layer, Nano Lett. 2 (2002) 329–332.

[41] T. Ramanathan, F.T. Fischer, R.S. Ruoff, Amino functionalized carbon nanotubes for binding to polymers and biological systems, Chem. Mater. 17 (2005) 1290–1295.

[42] K.A. Williams, T.M. Peter, B.G. Veenhuizen Torre, R. Eritja, C. Dekker, Nanotechnology: carbon nanotubes with DNA recognition, Nature 420 (2002) 761–762.

[43] W.W. Chen, C.H. Tzang, J.X. Tang, M.S. Yang, S.T. Lee, Covalently linked deoxy ribonucleic acid with multiwall carbon nanotubes–synthesis and characterization, Appl. Phys. Lett. 86 (2005) 3114 (Art No. 103114).

[44] W. Yan, D.W. Pang, S.F. Wang, Y.D. Zho, Carbon nanomaterials–DNA bioconjugates and their applications, Fullerenes, nanotubes, and carbon nanostructures 13 (2005) 309–318.

[45] M. Hazani, R. Naaman, F. Hennrich, M.M. Kappes, Confocal fluorescence imaging of DNA-functionalized carbon nanotubes, Nano Lett. 3 (2003) 153–155.

[46] B.J. Taft, A.D. Lazareck, G.D. Withey, A. Yin, J.M. Xu, S.O. Kelley, Site-specific assembly of DNA and appended cargo on arrayed carbon nanotubes, J. Am. Chem. Soc. 126 (2004) 12750–12751.

[47] E. Buzaneva, A. Karlash, K. Yakovkin, Y. Shtogun, S. Putselyk, D. Zherebetskiy, A. Gorchinskiy, G. Popova, S. Prilutska, O. Matyshevska, Y. Prilutskyg, P. Lytvyn, P. Scharff, P. Eklund, Mater. Sci. Eng. C 19 (2002) 41–45.

[48] G. Lee, C. Chen, T. Wang, W. Lee, Affinity chromatography of DNA on nonporous copolymerized particles of styrene and glycidyl methacrylate with immobilized polynucleotide, Anal. Biochem. 312 (2003) 235–241.

[49] N. Nakashima, S. Okuzono, H. Marakami, T. Nakai, K. Yoshikawa, DNA dissolves single-walled carbon nanotubes in water, Chem. Lett. 32 (2003) 465–466.

[50] M.J. Moghaddam, S. Taylor, M. Gao, S. Huang, L. Dai, J.M. McCall, Highly efficient binding of DNA on the sidewalls and tips of carbon nanotubes using photochemistry, Nano Lett. 4 (2004) 89–93.

[51] G. Lu, P. Maragakis, E. Kaxiras, Carbon nanotube interaction with DNA, Nano Lett. 5 (2005) 897–900.

[52] G.F. Cheng, J. Zhao, Y.H. Tu, P.A. He, Y.H. Fang, A sensitive DNA electrochemical biosensor based on magnetite with a glassy-carbon electrode modified by multiwalled carbon nanotubes in polypyrrole, Anal. Chim. Acta 533 (2005) 11–13.

[53] S.G. Wang, R. Wang, P.J. Sellin, Q. Zhang, DNA biosensors based on self-assembled carbon nanotubes, Biochem. Biophys. Res. Commun. 325 (2004) 1433–1437.

[54] S. Li, P. He, J. Dong, Z. Guo, L. Dai, DNA-directed self-assembling of carbon nanotubes, J. Am. Chem. Soc. 127 (2005) 14–15.

[55] S. Banerjee, S.S. Wong, Synthesis and characterization of carbon nanotube–nanocrystal heterostructures, Nano Lett. 2 (2002) 195–200.

[56] T. Belin, F. Epron, Characterization methods of carbon nanotubes: a review, Mater. Sci. Eng. B 19 (2005) 105–118.

[57] Y. Wang, Z. Iqbal, S.V. Malhotra, Functionalization of carbon nanotubes with amines and enzymes, Chem. Phys. Lett. 402 (2005) 96–101.

[58] C.A. Dyke, J.M. Tour, Solvent-free functionalization of carbon nanotubes, J. Am. Chem. Soc. 125 (2003) 1156–1157.

[59] R.K. Saini, I.W. Chiang, H. Peng, R.E. Smalley, W.E. Billups, R.H. Hauge, J.L. Margrave, Covalent sidewall functionalization of single wall carbon nanotubes, J. Am. Chem. Soc. 125 (2003) 3617–3621.

[60] J. Liquier, A. Akhebat, E. Taillander, F. Coolin, T.D. Huynh, J. Igolen, Characterization by FTIR spectroscopy of the oligoribonucleotide duplexes r(A-U)6 and r(A-U)8, Spectrochim. Acta A 47 (1991) 177–186.

[61] G.I. Dovbeshko, O.P. Repnytska, E.D. Obraztsova, Y.M. Shtogun, DNA interaction with single-walled carbon nanotubes: a SEIRA study, Chem. Phys. Lett. 372 (2003) 432–437.

[62] K. Jiang, A. Eitan, L.S. Schadler, P.M. Ajayan, R.W. Siegel, Selective attachment of gold nanoparticles to nitrogen-doped carbon nanotubes, Nano Lett. 3 (2003) 275–277.

[63] B. Kim, W.M. Sigmund, Functionalized multiwall carbon nanotube/gold nanoparticle composites, Langmuir 20 (2004) 8239–8242.

[64] K. Kerman, Y. Morita, Y. Takamura, M. Ozsoz, E. Tamiya, DNA-directed attachment of carbon nanotubes for enhanced label-free electrochemical detection of DNA hybridization, Electroanalysis 16 (2004) 1667–1672.

[65] M. Guo, J. Chen, D. Liu, L. Nie, S. Yao, Electrochemical characteristics of the immobilization of calf thymus DNA molecules on multi-walled carbon nanotubes, Bioelectrochemistry 62 (2004) 29–35.

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