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Organically Structured
Carbon Nanotubes for Fluorescence

Jianguo Tang and Qingsong Xu
[1]Institute of Hybrid Materials,
[2]Laboratory of New Fiber Materials and Modern Textile,
The Growing Base for State Key Laboratory,
[3]Department of Materials Science and Engineering, College of Chemistry,
Chemical and Environmental Engineering, Qingdao University, Qingdao
P.R. China

1. Introduction

Carbon nanotubes (CNTs), an one-dimensional (1D) nanostructural material, despite its inactivity, has the advantages of chemical flexibility and sensitivity arising from the susceptibility of their surfaces to interacting species. The researches emerged recently on functionalizing CNTs with functional organic macromolecules and oligomers have achieved novel light-emitting, light-electric or electric-light converting materials. In this chapter, we aim to capture recent advances and present our research achievements of rational design and chemical functionalization of CNTs for the purpose to obtain enhanced fluorescence property in the variety of organically modified structures, lanthanide-existed hybrid structures, polymer-embedded composites as well as the wide variety of applications for novel organic light-emitting diodes (OLEDs), laser resource, optical signal amplification, solar cells and biosensors. To provide a deeper understanding of the fluorescence property, this review will also survey the proposed mechanisms. As demonstrated by remarkable examples, the relationship between the structures of modified CNTs and the fluorescence property helps to offer attractive new prospects for constructing CNT-based molecular optoelectronic and photon devices with desired functionalities.

2. Organic modification chemistry of CNTs

Within the scope of this chapter, we shall focus on the fluorescence property of CNTs. Two main approaches are now considered for the surface modifications of CNTs. The first one is noncovalent attachment of functional molecules (NAFM) on to the walls of CNTs that is based mainly on van der Waals forces, controlled by thermodynamic parameters. NAFM can change the nature of CNTs surface and make it more compatible with different matrixes. The advantage of NAFM is that the perfect structure of the nanotube remains intact, and its mechanical properties also retain unchanged. However, its main disadvantage is that the binding forces between modification molecules and CNT surface might be too weak. The second approach is covalent attachment of functional molecules (CAFM). The functional molecules or oligomers can be attached on CNT surface via covalent bonds. It improves the

chemical interface bonding between modifiers and CNT surface and provides stable surface properties of modified CNTs. However, the modification methods will be complicated, compared with NAFM, and introduce defects on the walls of CNTs.

2.1 Noncovalent attachment of functional molecules (NAFM)

The endeavors to improve the poor surface properties have been started as early as CNTs' discovery in 1991[1]. So far there are lots of publications [2-4] focusing on the modifications of CNTs for their compatibility with solvents in solutions and with matrixes in solid materials. For functionalized fluorescent CNTs, a successful surface modification strategy on CNTs pursues not only the compatibility but also the structures to be extended for luminescent groups.

Although the solubility can be improved by covalent modification of the SWNTs [5,6], these methods can disturb the natural properties of SWNTs. Therefore, NAFM has its merits to obtain the non-damaged structures. The early reports of R. E. Smalley [6] and S. M. F. Islam [7] indicated the efficient solubilization of SWNTs can be achieved by using the noncovalent wrapping, adsorption, and encapsulation. In this review, we will give the comments on the related developments. Because SWNTs structured by NAFM organically offer a unique combination of electrical, mechanical, thermal, and optical properties [2,3], they make them highly promising materials for a huge number of applications [4] ranging from nanocomposites, solid-state nanoelectronics, sensors, biomedical devices, and cellular delivery [8].

2.1.1 Wrapping by oligomers

Molecular engineering (cutting, solubilization, chemical functionalization, purification, manipulation, and assembly) of single walled carbon nanotubes (SWNTs) will play a vital role in exploring and developing their applications. Noncovalent wrapping of carbon nanotubes, as shown in Figure 1, is of particular interest, because it enables one to tailor their properties while still preserving nearly all of the nanotube intrinsic properties. SWNTs have become solubilized in organic solvents and water after wrapped by oligomers.
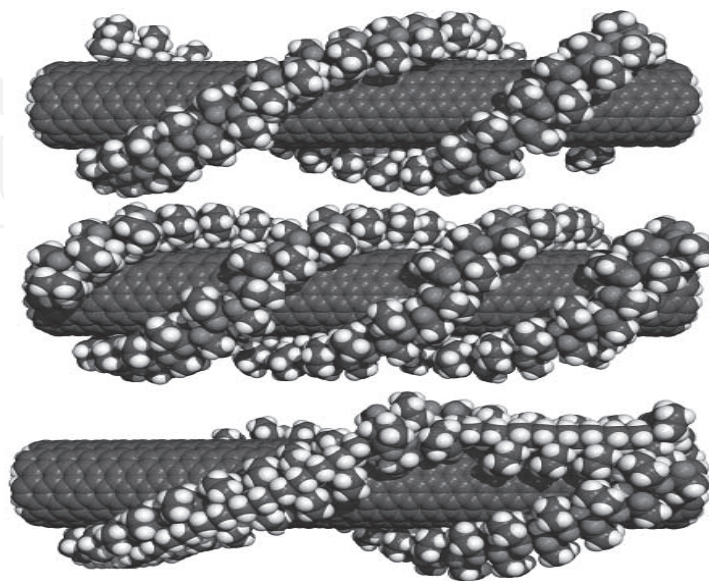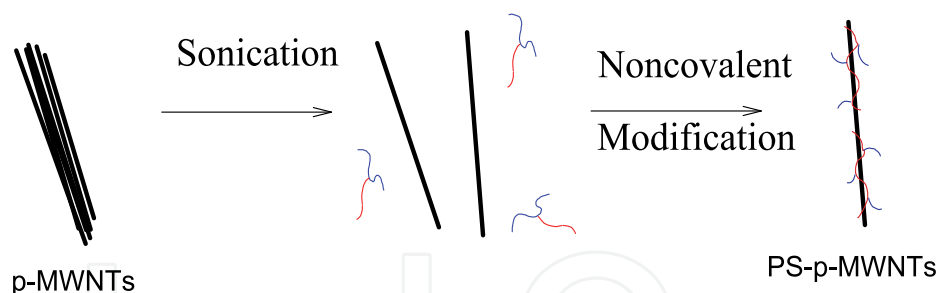

Fig. 1. Polymer wrapping [6]

Fig. 2. The noncovalent surface modification of pristine-MWNTs with PS-g-(GMA-co-St) [10]

A simple, nondestructive method to modify MWNTs with a graft polymer (PS-g-(GMA-co-St)) noncovalently has been shown in Figure 2. This strategy is based on the affinity of the poly(styrene)(PS) main chains to the surface of pristine MWNTs (p-MWNTs) [11, 12], and the modified MWNTs can be solubilized in a wide variety of polar and nonpolar organic solvents at the same time.

Recently, Gupta and his coworkers found a simple method to functionalize the CNTs with fluorescent ink noncovalently [13]. 1 mg of CNTs was stirred with 10 ml of dilute ink solution in water for 8 to 10 h and subjected to sonication afterwards for two hours. The extra insoluble CNTs were then removed by centrifuging at 1600g (3500 rpm) for one hour. The collected solution was found to be stable for a few months. One to two drops of the solution of functionalized CNTs was dispensed onto a carbon-coated copper grid (300 mesh) for a few seconds, and extra solution was soaked off with a filter paper. The composite shows spectroscopic features of the fluorescent ink indicating noncovalent bonding between the CNTs and the ink molecules. The results shown here throw light upon the feasibility of designing efficient nanocomposite materials via attaching well known optical materials to CNTs.

T. D. Krauss et al. reported significant increases in the fluorescence efficiency of individual DNA-wrapped SWNTs upon addition of reducing agents, including dithiothreitol, trolox, and β-mercaptoethanol [14]. Brightening was reversible upon removal of the reducing molecules, suggesting that a transient reduction of defect sites on the SWNT sidewall caused the effect. These results implied that SWNTs were intrinsically bright emitters and that their poor emission aroused from defective nanotubes.
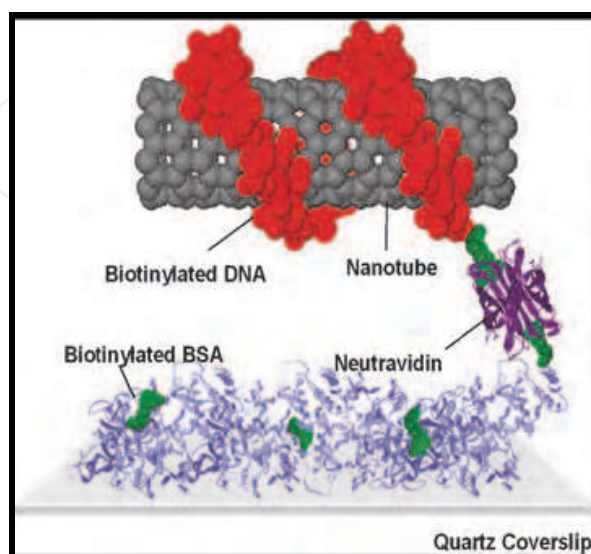

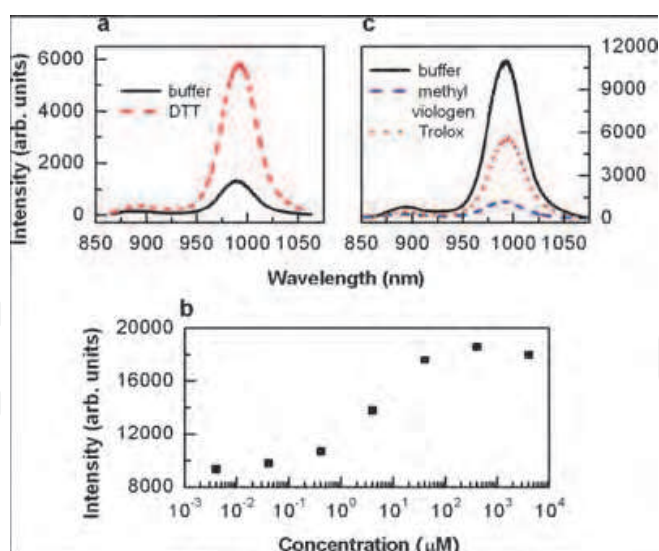Fig. 3. Sample configuration for fluorescence measurements of individual SWNTs[14].

Fig. 4. Enhancement and quenching of fluorescence intensity for SWNT ensembled by reductants and oxidants. (a)Fluorescence spectra for an ensemble of SWNTs, displaying the enhancement of the fluorescence intensity upon addition of DTT. (b) Saturation curve of SWNT fluorescence intensity for increasing concentrations of added Trolox. (c) Fluorescence spectra for an ensemble of SWNTs measured in buffer, with addition of methyl viologen and with addition of Trolox[14].

Short, rigid conjugated polymers, poly (aryleneethynylene) s (PPE) (Figure 5), are used to solubilize SWNTs [15]. In contrast to previous work [10], the rigid backbone of PPE cannot wrap around the SWNTs. The major interaction between polymer backbone and nanotube surface is most likely π-stacking. This approach allows to control over the distance between functional groups on the carbon nanotube surface, through variation of the polymer backbone and side chains. This approach represents the carbon nanotube solubilization via π-stacking without polymer wrapping and enables the introduction of various neutral and
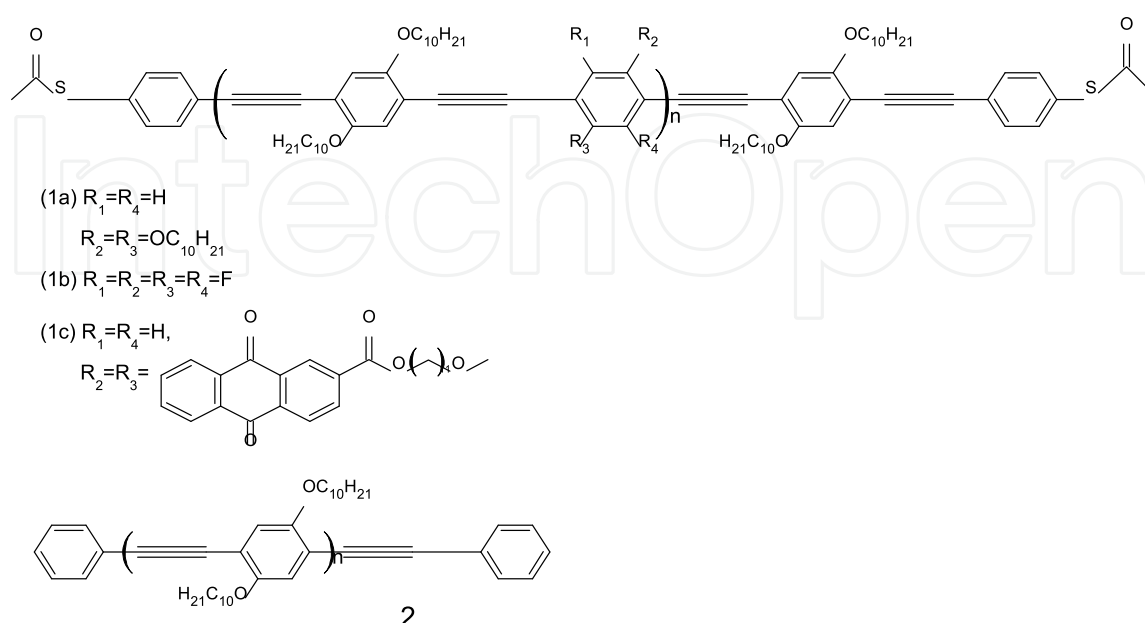

Fig. 5. Molecular structures of poly (aryleneethynylene) s (PPE) [15]

ionic functional groups onto the carbon nanotube surface. The optical spectroscopy supports a significant π-π interaction between the polymer and the nanotube (Figure 6). The strong fluorescence of 1a is efficiently quenched in 1a-SWNTs$_{HiPCO}$. The quenching likely arises from efficient energy transfer between 1a and SWNTs, rather than the disruption of π-conjugation caused by a conformational change.

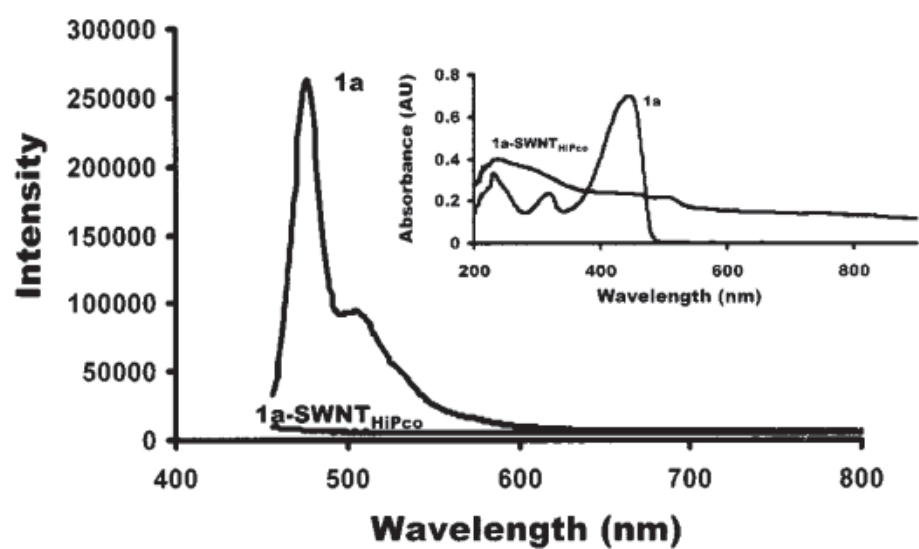| PPE ($n_{average}$)	avg length (nm)	SWNT$_{Hipco}$ Solubility (mg/mL)
1a(19.5)	27.9	~2
1a(13)	19.6	~2.2
2(16)	12.0	~2
2(10)	7.9	~1.5

Fig. 6. Room temperature solution-phase (CHCl$_3$) fluorescence spectra (excitation wavelength: 400nm) and UV-visible spectra (inset) of 1a and 1a-SWNTs$_{HiPco}$ complex [15].

B. X. Li and coworkers had developed a new multicolor fluorescent sensing system to detect multiple analytes in one pot [16]. This design was built on the noncovalent assembly of dye-labeled aptamer with SWNTs by π-stacking between the nucleotide bases and the SWNTs sidewalls. That is to say, they combine the highly specific binding ability of aptamers with the ultrahigh quenching ability of SWNTs to develop a multicolor fluorescent sensing system. This multicolor fluorescent system is used to simultaneously detect thrombin and ATP in a single solution.

C. Fantini et al. carried on an insightful research on the influence of the nanotube and surfactant concentrations on the absorption and emission of light by individualized CNTs [17]. SWNTs dispersed in different surfactant solutions and at different concentrations were investigated by optical absorption and photoluminescence, aiming to investigate how higher photoluminescence efficiency (emission/absorption ratio) can be obtained for SWNT dispersion by choosing the type of surfactant and controlling the SWNT and surfactant concentrations. The result showed that the concentrations whose best efficiency of PL measurements was obtained correspond to the dispersions with higher ratio between individually dispersed nanotubes and bundles.

2.1.2 Adsorption of semiconductor nanoparticles

Because of their unique size-tunable chemical and physical properties, semiconductor nanoparticles have attracted much attention. Several semiconductor nanoparticles such as Ag_2S, CdS, have already been bound to the surfaces of CNTs. Metal sulfides, as one kind of important semiconductors, have been used in many new application areas, such as laser communication and light-emitting diodes. Metal sulfides nanoparticles such as Ag_2S and CdS with size of less than 30 nm are coated onto MWNTs successfully by a simple and effective in situ synthetic method without severely affecting the energy states of the MWNTs (Figure 7) [9]. This method could be extended to other transition metal compound nanostructures. This new type of hybrid carbon nanotubes with coated metal sulfides nanoparticles on the sidewall may have more interesting potential applications in field emitters, nanometer-scale optoelectronic devices and other related sides.
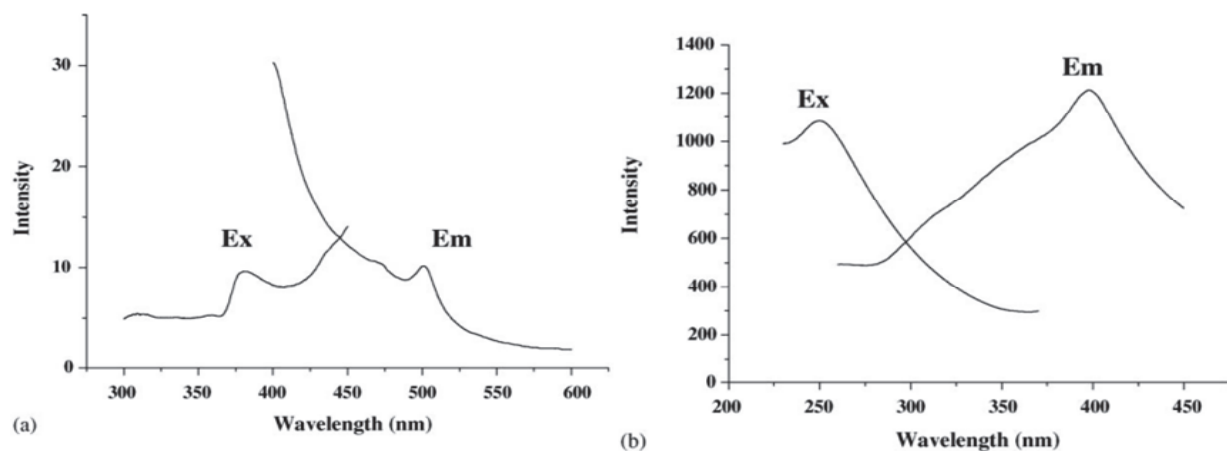

Fig. 7. Emission and excitation spectra of (a) CdS/MWNTs, (b) Ag_2S/MWNTs [9]

2.1.3 Noncovalent encapsulation

Filling its interior cavity with other molecules is another novel means to modify the properties of a SWNT. For example, SWNTs filled with 1-D chains of C_{60}, can be manufactured via a vapor phase or surface diffusion mechanism. The presence of interior C_{60} could decrease the SWNTs compressibility and increase its elastic modulus, which has been shown by molecular dynamics simulation. The method of encapsulation has been extended to other related molecules such as metallofullerenes La_2-C_{80} and Gd-C_{82}. The case of La_2-C_{80}-SWNT is regarded as the definitive proof that a non-intrinsic molecule could be inserted in bulk into SWNTs [18].

2.2 Covalent Attachment of functional molecules (CAFM) or oligomers (CAFO)

We can find in recent reports on the chemical compatibility and dissolution properties of CNTs that most researchers put special emphasis on developing modifications or functionalizations of their surface. When tailoring the properties of these materials and the engineering of nanotube devices, the modification chemistry of the open ends, the exterior walls, and the interior cavity of the CNTs is expected to play a vital role. Until now, several methods have been applied to graft or assemble synthetic oligomers, polymers or biomacromolecules onto the exterior surface of CNTs using covalent bonds.

Chemical modification of the SWNTs, as well as the MWNTs, has been carried out with a mixture of sulfuric acid and nitric acid, which is used to form carboxyl acid groups on the

surface. The resultant carboxylic acid groups are formed along the nanotube walls and the ends. Then, we could attach the desired groups to the exterior walls by the reaction between the groups and the carboxyl acid groups.

2.2.1 Reactions with carboxyl groups on CNTs

The surface modification of MWNTs using highly branched molecules covalently attached onto the surface of MWNTs has been developed, which proves to be a representative example for the modification of CNTs by reacting with the carboxyl groups on the sidewall. The general strategy for modification is described in Figure 8. During this process, the volume of the MWNTs expands several times, perhaps because of exfoliation of the MWNTs bundles to give individual nanotubes.
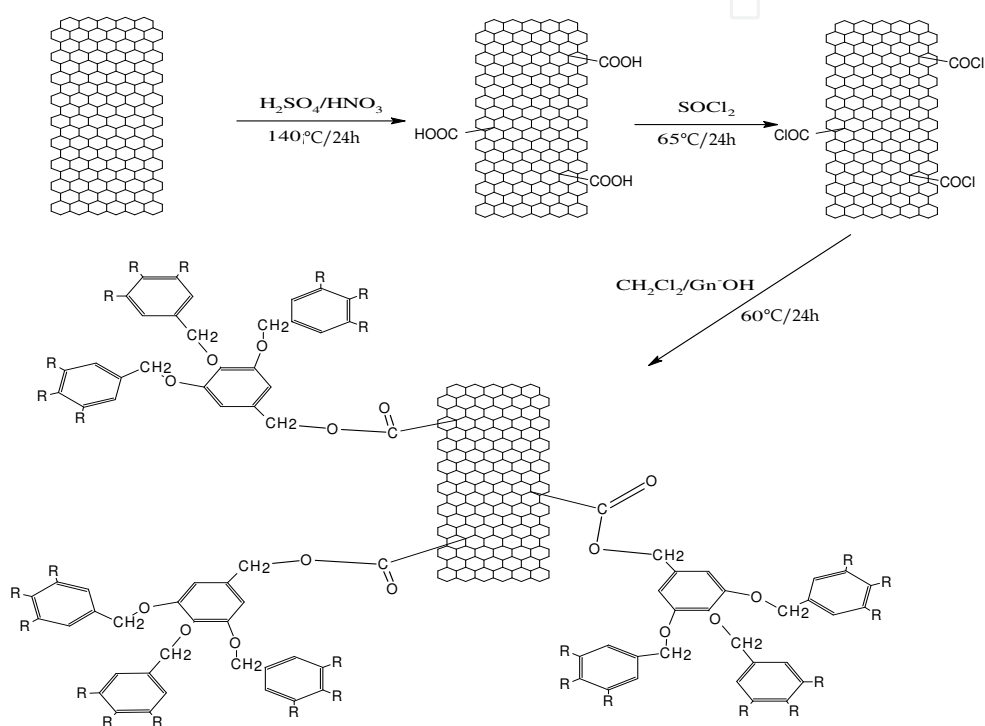

Fig. 8. A method of surface modification of multiwalled carbon nanoparticles (MWNTs) using highly branched molecules covalently attached onto the surface of MWNTs [19].

The MWNTs with carbonyl chloride groups (MWNT-COCl) were prepared via reaction of thionyl chloride with carboxyl-contained MWNT (MWNT-COOH) previously made by oxidation of the raw MWNT [20]. After centrifugation, the brown-black supernatant was decanted and the remaining solid was washed with anhydrous tetrahydrofuran (THF). After centrifugation, the pale yellow-colored solution was decanted. The remaining solid was then dried at room temperature in vacuum. An anhydrous dichloromethane (CH_2Cl_2) mixture of MWNT-COCl and 0.5 g poly(benzyl ether) highly branched molecules was heated at 60℃ for 24 h. After cooling to room temperature, the excess highly branched molecules are removed by washing with ethanol for four times (5 to 10 min sonication at 40 kHz). The remaining solid is dried at room temperature under vacuum. The yield of resultant product is usually >60% (based on raw MWNTs). In summary, MWNTs can be successfully modified with highly branched molecules by reaction of carbonyl chloride groups functionalized MWNT (MWNT-COCl) and highly branched molecules that have hydroxyl groups at the focal point. The

modification of CNTs may provide valuable properties in many application areas such as optoelectronics, information storage, and catalysis [19].

The first study on functionalization of SWNTs with enzymes has already been achieved by the initial acylation of SWNTs followed by amidation with the desired amine or enzyme [21]. The two-step chemical method needs mild conditions and results in tethering of the organic functionality through a covalent bond [Figure 9]. It is a simple, but practical and highly effective process. The two enzymes tethered to SWNTs are porcine pancrease lipase (PPL) and amino lipase (AK). The same method is also used to functionalize SWNTs with various amines, which include three primary amines (cis-myrtanylamine, 2, 4-dinitroaniline, 2, 6-dinitroaniline) and two secondary amines N-decyl-2, 4, 6-trinitroaniline and N-(3-morpholinopropyl)-2, 4, 6-trinitroaniline. Linkage of chiral molecules and enzymes to SWNTs further makes the applications of CNTs possible in areas such as medicinal and biological fields, biosensor or chemically modulated nanoelectronic devices. Tethering to nitrated molecules is also hoped for the use of SWNTs in nanoscale energetic systems.
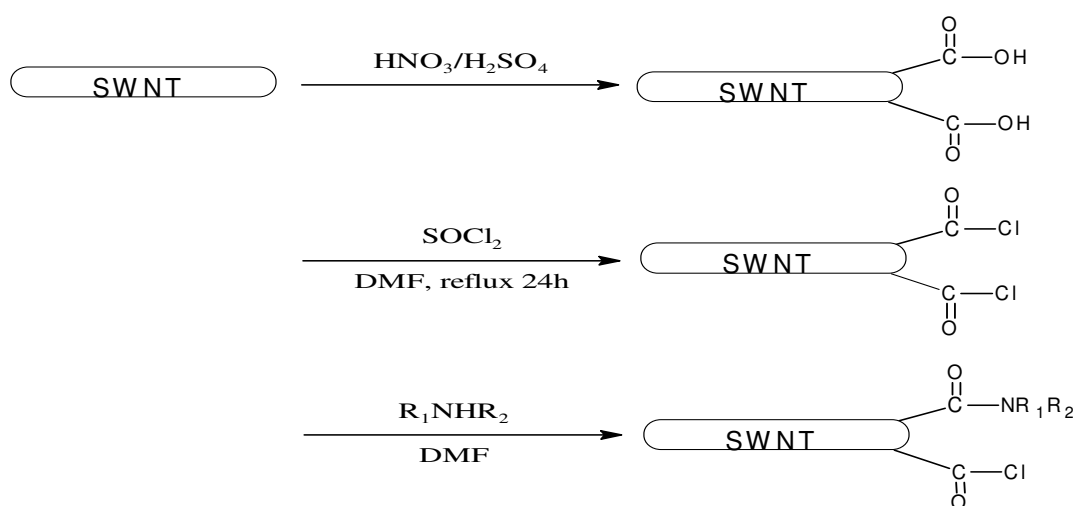

Fig. 9. CNTs modification with amines and enzymes [21]

The exact functional groups of R_2 for different functionalizations are those compounds, such as 2, 4-dinitroaniline and N-decyl-2, 4, 6-trinitroaniline, while the R_1 is mainly hydrogen.

Both MWNTs and SWNTs have been considered as attractive candidates for fabricating novel materials with desirable properties, owing to their tubular nanostructures, unique and promising mechanical properties. However, compared with MWNTs, SWNTs exhibit simpler structures and are easier to control as regards diameter during fabrication, so most previous academic researches on CNTs are focused on SWNTs. However, as noted by Dalton et al. [22], the high cost of SWNTs severely hindered its commercialization for most applications severely. This problem can be released by using MWNTs, which have been scaled up recently in the industrial scale, resulting in a relatively lower price. Most of the excellent properties and merits of MWNTs are comparable with those of SWNTs. Therefore, it is desirable to pay more attention to MWNTs, particularly as regards functionalization, in the future.

Chemical (covalent) functionalization has been achieved through ultrasonication with organic materials [23], diimide-activated amidation, and 1, 3-dipolar cyclo additions, which we are going to introduce later [24]. End-to-end and end-to-side SWNT interconnects are formed by reacting chloride terminated SWNT with aliphatic diamine [25].

European scientists first reported their approach to covalently attach an inorganic metal complex to MWNTs [26] [Figure 10]
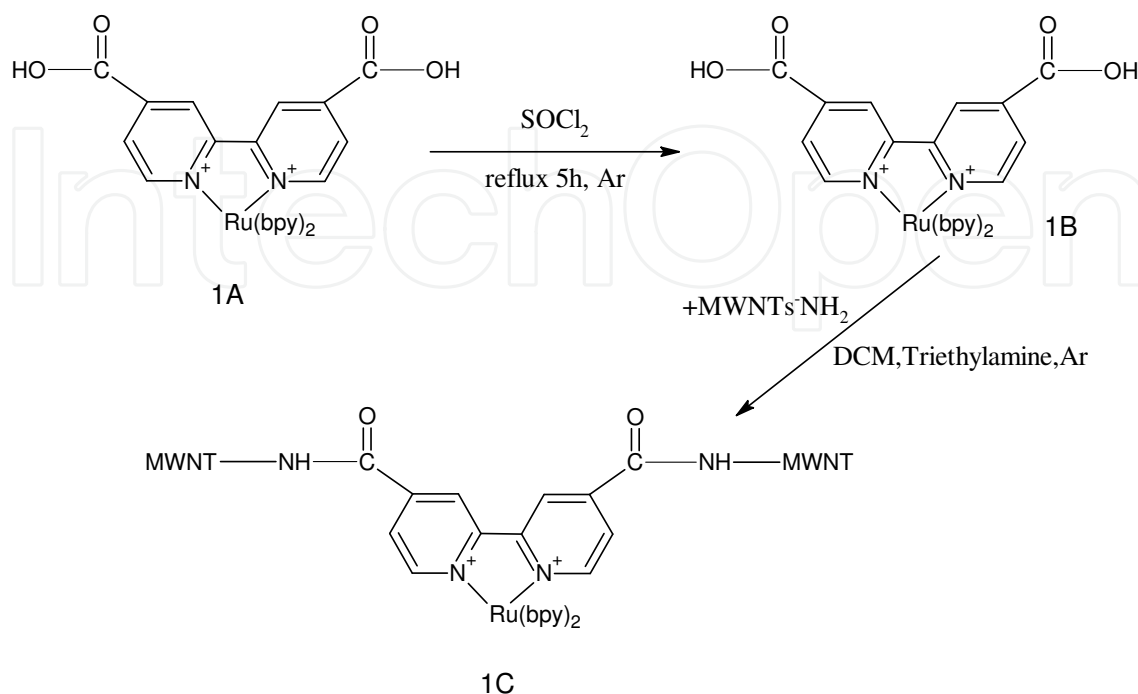

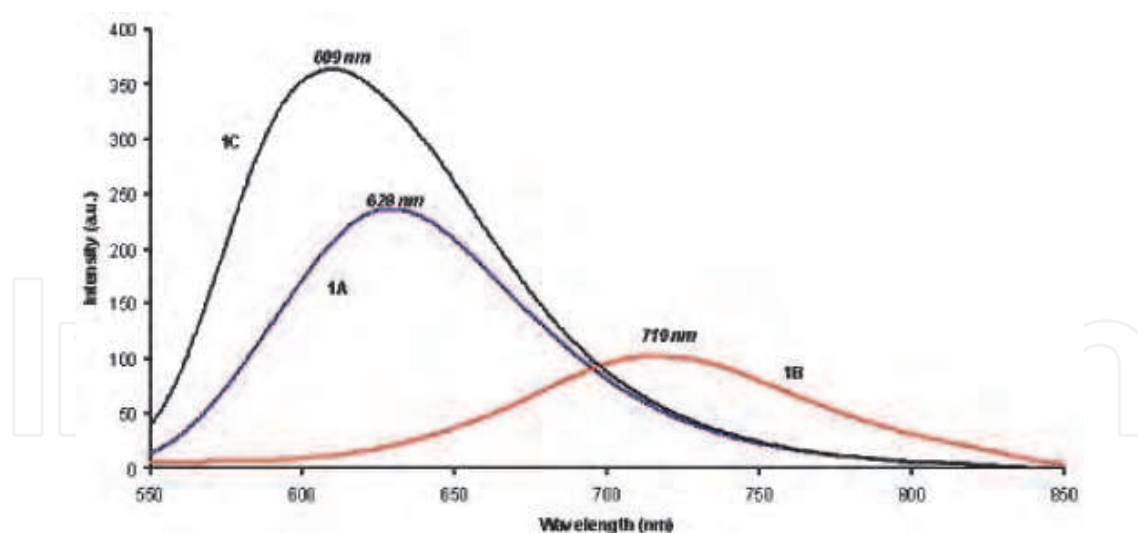Fig. 10. Connecting CNTs with an Inorganic Metal Complex [26]

Fig. 11. Emission spectroscopy (recorded in dichloromethane) on Ruthenium complex (1A), chlorinated product (1B), and Ruthenium nanotube complex (1C) [26].

The experimental procedure is shown in Figure 10. Ten milligrams (0.011 mmol) of [Ru(dcbpy)(bpy)$_2$](PF$_6$)$_2$ (1A) was dissolved in 15 ml of thionyl chloride. The reaction mixture (1B) was refluxed under argon for 5h. The thionyl chloride was then removed by vacuum distillation. The remaining solid was partially dissolved in dichloromethane (DCM). Two milligrams of the MWNT functionalized with NH$_2$ (MWNT-NH$_2$) was

sonicated in 5 ml of dichloromethane for 2 min and then were added to the refluxed mixture. Ten milliliters of triethylamine were added. The solution mixture was stirred at room temperature under argon for 72 h. Then, the product would be filtered to remove the solvents and washed with DCM. The product was placed in 20 ml of DCM and sonicated for 2 min. At last, the solution was allowed to settle for 24 h. Excess MWNT-NH_2 settled at the bottom, and the "functionalized ruthenium MWNT" (1C) product was in suspension in solution. A color change from dark red-orange (1B) to dark brown-green (1C) would be observed after the completion of the reaction scheme [Figure 11] [26].

Strong evidences by emission spectroscopy had been presented, which confirmed the successful creation of MWNTs interconnection through amide linkage with a ruthenium complex [26] [Figure 11].

2.2.2 Reactions with other groups on CNTs

MWNTs can be functionalized and solubilized via attaching aminopolymers to the CNTs [27], making it soluble in certain solvents. The acylation-amidation method and the direct heating method are both effective for this kind of functionalization, just as shown in Figure 12. The aqueous solubility of these functionalized samples as a result of the hydrophilicity of the aminopolymers may find applications in introducing CNTs into biologically significant systems.
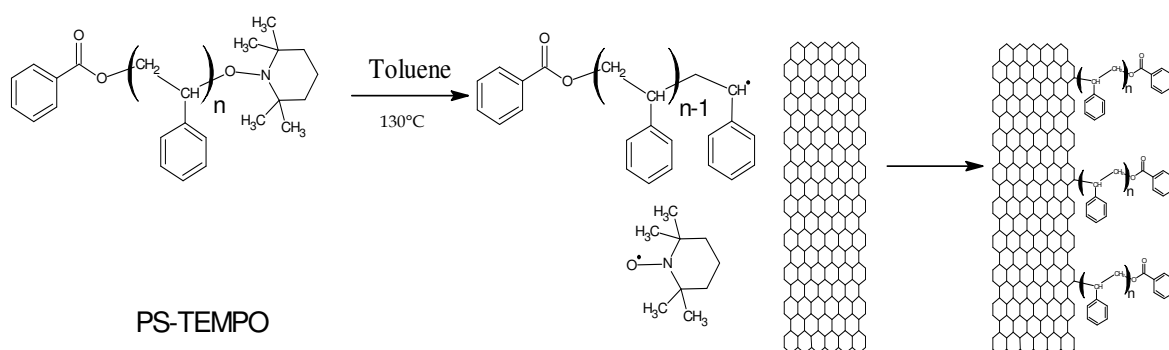

PS-TEMPO

Fig. 12. A strategy to graft alkoxyamine end-capped (co)polymers onto MWNTs [28]

Additionally, MWNTs have been modified by PS, PCL, and PCL-b-PS as results of the addition reaction of the parent polymeric radicals. Grafted MWNTs can easily be dispersed in solvents such as toluene and THF with the help of these grafted polymers [28].

A general route for the 1, 3-dipolar cycloaddition of azomethine ylides functionalization of nanotubes is described in Figure 13. Derivatives on the substituents of either the aminoacid or the aldehyde may lead to numerous structurally different functionalized CNT materials which are potentially useful in diverse applications on nanotechnology.

Modified SWNTs are bonded like bundles or ropes with the diameter of about 50-100 nm and the length of several micrometers. Every rope consists of small bundles of two or three nanotubes, or even an individual isolated nanotube. In contrast, pristine SWNTs are usually bonded in bundles with an average diameter of 10 nm.

The development on architectural superstructures in the level of nanometer has become possible with the help of spontaneous self-assembly of structurally different fulleropyrrolidines. Numerous novel materials such as the organic functionalized nanotube derivatives or nanocomposites mentioned above can be synthesized, with a wide variety of properties resulted from the attached functional group.

SWNTs or MWNTs

R_1NHCH_2COOH, R_2CHO

DMF, 130°C
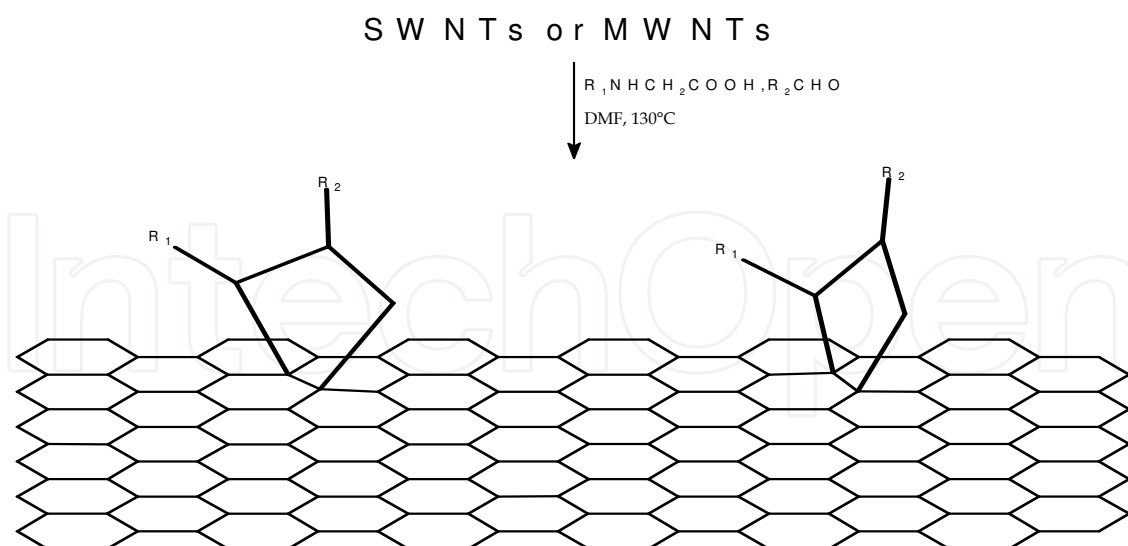
R_2

R_1

R_2

R_1

Fig. 13. Modification of nanotubes via 1, 3-dipolar cycloaddition of azomethine ylides [29].

Japanese researchers presented a method for simultaneously solubilizing and labeling CNTs by using a detergent covalently coupled with a variety of fluorophores commonly used in biology [30]. Because of their stability under physiological conditions and their varying fluorescence properties, fluorescently labeled nanotubes can be easily utilized in combination with biomolecules such as proteins.

2.2.3 New approach to the modification of CNTs

Just as mentioned earlier, functionalization of CNTs is advantageous to prevent the aggregation of nanotubes and to favor their solubilization in organic solvents at the same time [31, 32]. The attached functional groups can be used as precursors for the subsequent attachment of a wide variety of other functional groups [33]. To obtain functionalized nanotubes, direct fluorination by F_2 gas is a method widely used, which is known to be very corrosive, making the reaction difficult to handle. Besides, it is shown that fluorine can attack the nanotubes over 50°C, and at higher temperatures some undesirable reactions may take place [33, 34]. The average length of nanotubes after the preparation step is usually much higher than their diameter, which makes them unsuitable to be used as a nanometer-scale material [35]. The nanotubes whose length/diameter ratio is too high to be used as electron emitters are also difficult to disperse in polymer matrices. Boiling in oxidative media or grinding in a ball mill can effectively reduce the length of CNTs [35-37]. Compared to other shortening methods such as ultrasound power or STM voltage, by ball milling we can obtain shortened nanotubes in large quantities. Ko'nya et al. performed the functionalization of multi-walled carbon nanotubes by ball milling in reactive atmospheres (H_2S, NH_3, Cl_2 etc.) and proved that this method was appropriate for large scale production of short functionalized nanotubes [38]. Recent research has carried out the functionalization of SWNTs in an agate ball mill by using trifluoromethane (TFM), trichloromethane (TCM), tetrachloroethylene (TCE), hexafluoropropene (HFP) and chlorine (Cl_2), which had demonstrated that ball milling of single-walled carbon nanotubes in reactive atmospheres was an effective method in large-scale production of functionalized short SWNTs.
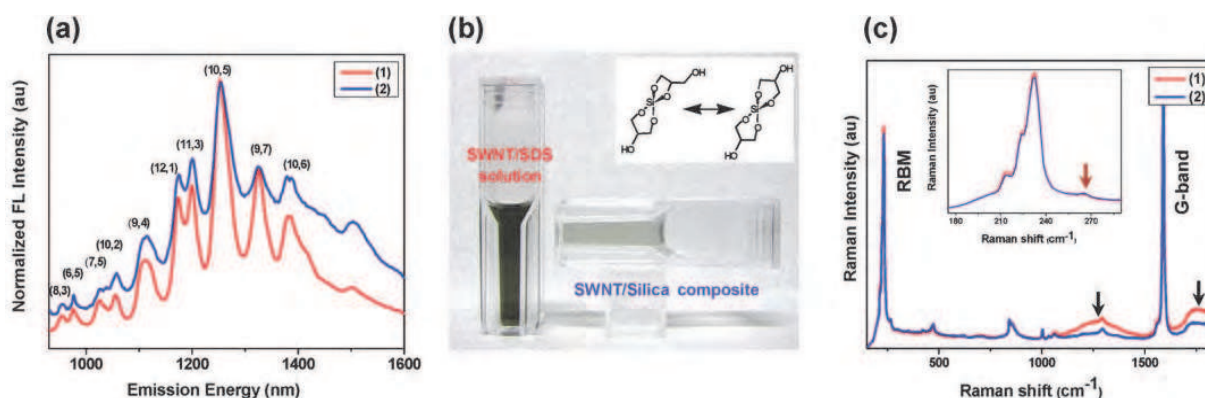
Fig. 14. (a) Normalized fluorescence spectra recorded on (1) SWNT/SDS dispersion in D_2O and (2)SWNT/silica monolith prepared using the SWNT/SDS solution shown in (1); (b) Photograph showing a SWNT/SDS aqueous dispersion (upright cuvette) and a SWNT/silica monolith (tilted cuvette). Inset showed the possible molecular structures of the silica precursor DGS; (c) Raman spectra of (1) a SWNT/SDS dispersion in D_2O and (2) a SWNT/silica monolith. Inset showed the radial breathing mode (RBM) spectra of the samples [40].

It was shown that alkyl-halides were suitable for substitution of very corrosive fluorine and chlorine gases in the process of functionalization of carbon nanotubes [39]. A. M. Dattelbaum and his coworkers had developed a new approach for the preparation of SWNT/silica composite materials, which were fluorescently active [40]. This approach made use of diglyceryl silane, a sugar alcohol based silica precursor molecule, which would condense under conditions that did not promote significant aggregation of the surfactant-nanotube assemblies, as was shown by fluorescence and Raman spectroscopy [Figure 14].
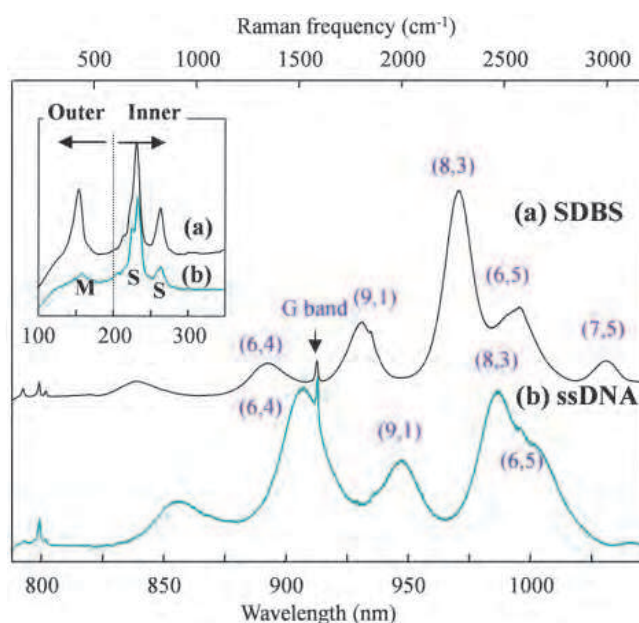

Fig. 15. Comparative Raman/fluorescence spectra taken with laser excitation of 785 nm for SDBS and DNA-dispersed DWNT supernatants. The inset showed the magnified low frequency Ramen spectra, where M indicated metallic and S indicated semiconducting tubes. [42]

Double-walled carbon nanotubes (DWNTs), have attracted a great deal of attention due to their intrinsic coaxial structures make them mechanically, thermally, and structurally more stable than SWNTs[41]. Kim et al. reported for the first time, detailed Raman/luminescence spectroscopic studies on single-standard DNA-dispersed DWNT solutions at different dispersion states [42], in comparison with an SDBS-dispersed DWNT solution using three different laser lines, in order to understand the interactions between DNA and the outer tubes, and the effect of these different DWNT environments on the vibrational and luminescence behaviors.
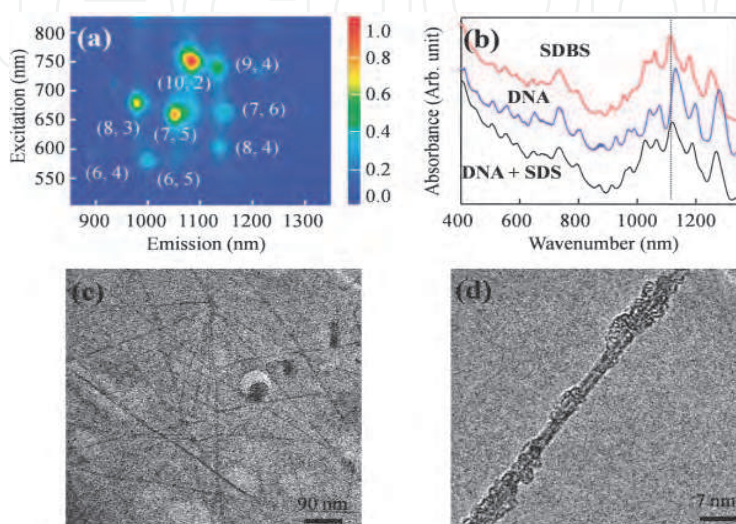

Fig. 16. (a) PL map and (b) UV/visible absorption spectra of DNA-dispersed DWNT solution at pH=8.0,(c,d) their corresponding TEM images. Note that DWNTs are individualized with the help of help of helically wrapped DNA. Their color represented the PL intensity on a linear scale. [42]

3. Fluorescent CNTs grafted by fluorescent groups

CNTs are now attracting more and more attentions because of their high potentials in exploring novel nanoscale electronic and optical devices. For example, room temperature single electron transport devices have been developed which are expected to be the building block of integrated circuits in the future. Artificial atoms have also demonstrated their use in quantum computing. It has also been shown that semiconducting SWNTs can emit light from visible to infrared spectral region and light-emission based on current injection has been demonstrated, all of which arise the study on optical properties of SWNTs. It has been found that the exciton binding energy in a CNT is as large as 0.4 eV, several tens of that of a traditional semiconductor. Large nonlinearity has also been found in SWNTs [43]. With rising temperature, suspended SWNTs exhibit discontinuous changes in their emission energy which is much different compared to a traditional semiconductor. These results show that more efforts are still needed to discover the novel physical and optical properties of CNTs.

As mentioned earlier, the insolubility of nanotubes in most solvents has hindered quantitative investigations. A feasible way to solubilize carbon nanotubes is to covalently attach them to highly soluble linear polymers. An interesting finding has been reported that the polymer-bound CNTs in homogeneous organic and aqueous solutions are luminescent or even strongly luminescent.

Shortened MWNT (S-MWNT), shortened SWNT (S-SWNT) and SWNT samples were treated with HCl solution to fully recover the carboxylic acid groups on the surface of CNTs, and refluxed in $SOCl_2$ for 24 h to convert the carboxylic acids into acryl chlorides. These functionalized CNTs were then mixed with poly-(propionylethylenimine-co-ethylenimine) (PPEI-EI, $M_W \approx 200000$, EI mole fraction$\approx 15\%$) and reacted at 165°C for 20 minutes. The reaction mixtures were repeatedly extracted with chloroform to obtain the soluble fractions, which were then purified via repeated precipitations. It appeared that the polymer attachment is at the end of nanotube, as illustrated in Figure 17.
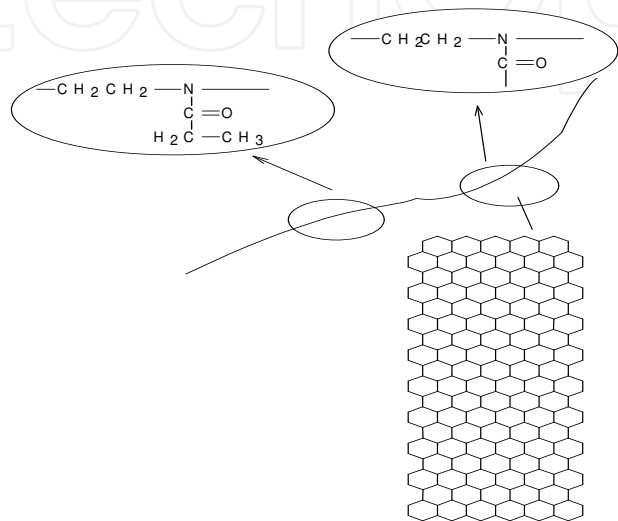

Fig. 17. An illustration of the PPEI-EI polymer-bond carbon nanotubes [44]

sample	solvent	λ_{EX}(nm)	Φ^a	τ_1(ns)	τ_2(ns)	a_1/a_2
S-MWNT−PPEI-EI	CHCl₃	632		2.2	5.6	1.2
		400	0.11	2.3	8.0	2.9
S-SWNT−PPEI-EI	Water	400	>0.03	2.3	8.9	4
	CHCl₃	632		1.9	5.8	1.2
SWNT−PPEI-EI	CHCl₃	440	0.06			
		400	>0.003	1.5	7.3	4.2
S-MWNT−PVA-VA	Water	365		2.1	9.8	2.3
	CHCl₃	365	>0.03	1.6	6.0	7.3

Table 1. Luminescence Parameters of the Polymer-Bond Carbon Nanotubes in Solution [44]

The same reaction conditions were used to attach S-MWNT to poly (vinyl acetate-co-vinyl alcohol) (PVA-VA, MW≈110 000, alcohol mole fraction≈40%) via ester linkages [45, 46]. These samples of polymer-bound CNTs were soluble in both organic solvents and water, forming highly colored homogeneous solutions. After being repeatedly filtered through 0.2 µm

Teflon filters, the chloroform and aqueous solutions were used for spectroscopic measurements. UV/vis absorption spectra of the chloroform solutions at room temperature (~22°C) are compared in Table 1, and spectra of the aqueous solutions are similar. The band-gap of fluorescence of semiconducting SWNTs in the near-IR is very sensitive to surface chemistry and often attenuated upon doping and functionalization, as is already known in the literature [47, 48]. On the other hand, the functionalized CNTs do show significant emission in the visible when excited at a shorter wavelength. The emission intensities and quantum yields can be very high, with yields of 4.5% and 3% for the spectra of PPEI-EI-SWNT and PEG$_{1500N}$-SWNT, respectively, shown in Figure 18. The luminescence decays are mostly nonexponential but generally fast, with the scale of a few nanoseconds [49, 50]. The decay results suggest inhomogeneity in the emitting species and the excited states responsible for the observed emissions. The excitation wavelength dependence, with the observed emission spectra progressively moving toward the red with longer excitation wavelengths, is consistent with the presence of significant inhomogeneity.
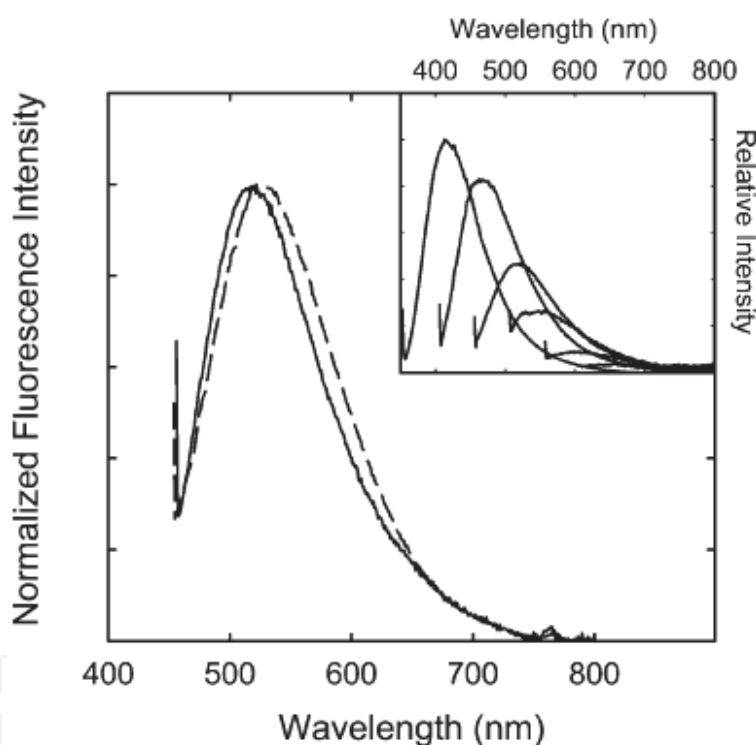

Fig. 18. Luminescence emission spectra (normalized, 450 nm excitation) of PPEI-EI-SWNT (—) and PEG$_{1500N}$-SWNT (- - -) in aqueous solution [50]. Inset: the spectra of PPEI-EI-SWNT excited at 350, 400, 450, 500, 550, 600 nm (intensities shown in relative quantum yields).

This is demonstrated well in a comparison of the visible luminescence emissions between purified nanotubes dispersed in a stable suspension with the aid of polymers and functionalized nanotubes in solution. While the two samples appear indistinguishable and are of similar absorption spectra and optical densities at the excitation wavelength, the observed luminescence emission intensities are very different. As compared in Figure 19, the solution of functionalized SWNTs is considerably more luminescent, which maybe due to the fact that more SWNTs are dispersed at individual nanotube level in the functionalized sample.
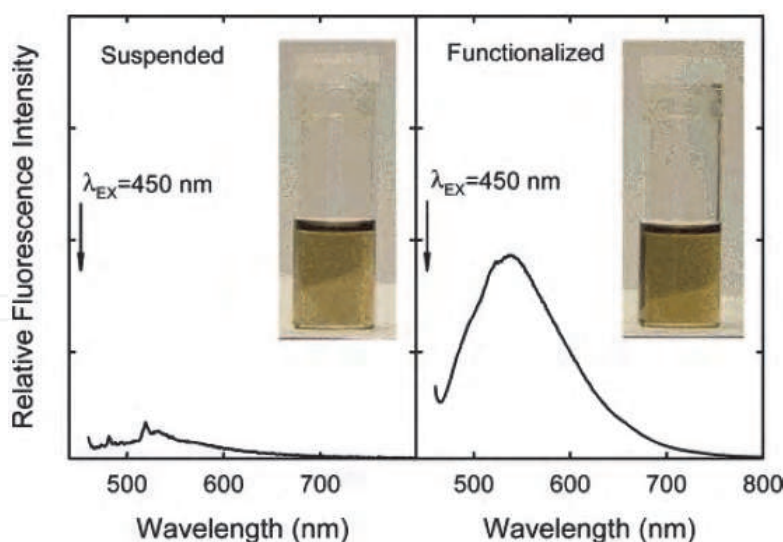
Fig. 19. Luminescence emission spectra from SWNTs dispersed with the aid of polyimide in DMF (left) and the polyimide-functionalized SWNTs (PI-NH$_2$-SWNT) in DMF solution (right) [50].

That is to say, there are strong luminescence emissions from well-dispersed CNTs in most functionalized samples. The broad luminescence emissions are logically owing to the trapping of excitation energy by defect sites in the nanotube structure, which are passivated upon the appropriate functionalization of the nanotubes. The better the dispersion and functionalization of the nanotubes, the more intense the luminescence emissions.

It is well known that the bleaching of nanotube fluorescence and absorbance spectra from the reaction of surfaced SWNTs with small organic electron-acceptor molecules depends solely on the reduction potential of the organic molecule. Thus, SWNTs can be perceived as behaving in a manner similar to that of other fluorescent organic molecules [51]. Metal ions have been used in emission studies to quench the fluorescence of various organic molecules including pyrenes, anthracenes, flavins, bipyridines, and acridinium ions [52-55]. However, no work before has focused on the interactions between SWNTs and metal ions. In order to further explore this phenomenon and determine the generality of M^{n+} quenching of SWNT fluorescence, A. R. Barron et al. had investigated the charge-transfer reaction between sodium dodecylbenzen-sulfonate(SDBS) surfaced SWNTs with group 2, 12, and 13 metal ions[51]. They found that the larger the ionic radii (lower the charge density) of the ion, the greater the efficiencies of quenching the smaller the SWNT, the greater the quenching effect of a particular M^{2+} ion.

K. J. Ziegler et al. reported a general method for coating SWNTs with polymer using emulsion-like microenvironments surrounding SWNTs [56]. Nylon 6, 10 were chosen as model systems for in situ emulsion polymerization. The reaction was going on at the surface of the nanotube, resulting in a thin polymer coating around individual SWNTs. The nylon-coated SWNTs were easily redispersed in water after freeze-drying. The fluorescence intensity of the nylon-coated SWNTs remains high at both acidic and basic pH conditions.

4. Polymer embedded CNTs with fluorescence emission centers

The use of polymers that are structurally close to the matrix polymer for the functionalization of CNTs is a favorable strategy in the development of polymeric carbon

nanocomposites. It ensures compatibility of the functionalized CNTs with the polymer matrix to avoid any potential microscopic phase separation in the nanocomposites. Generally speaking, the species used in the functionalization and solubilization of CNTs become "impurities" in the final nanocomposites. Some units in polymers, such as derivatized styrene units in the polystyrene copolymers, which are structurally closed to the matrix polymers, are also regarded as impurities. Thus, an ideal polymeric carbon nanocomposite may be prepared by using solubilized CNTs which are functionalized with the matrix polymer. One of the polymer systems that can be used for such a purpose is poly (vinyl alcohol) (PVA) [Figure 20]. PVA is an excellent matrix polymer for nanocomposites.
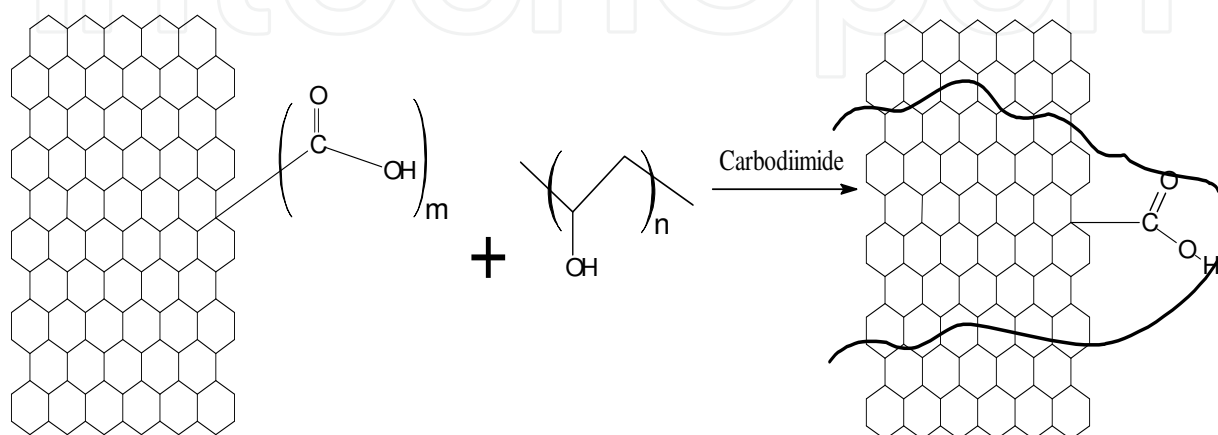

Fig. 20. Functionalization of CNTs with PVA [57]

The brief strategy of this kind of functionalization is shown vividly in Figure 20. Both SWNTs and MWNTs are functionalized with PVA in carbodiimide-activated esterification reactions. [58]

The PVA-CNTs composite films have high optical qualities, without any observable phase separation. The characterization results of the nanocomposite films show that the dispersion of CNTs is as homogeneous as that in solution.

There are studies which described an approach to the use of CNTs to pattern a high molecular weight polymer [Figure 21] [59, 60]. The resulting order of the attached polymer across the tube is surprising and seems to reflect the structural perfection of the tube itself. This templating of crystalline polymer suggests the possibility of constructing uniquely ordered, chemically tailored, and nanostructured materials in bulk from CNTs. The possibilities for such materials are numerous, from simple attachment to a polymer matrix material for enhancing yield strength to the construction of larger polymeric architectures with order over many different length scales. In this approach, MWNT and SWNT nanotubes are used as the beginning or templating nanomaterials [59].

The attachment between CNTs and the polymer results in a highly ordered polymer around the nanotubes, which provides us with a first step toward more complex construction using these nanomaterials. Dissolution of CNTs and the study of their properties in solution have been challenges for chemists. Although some efforts have been made in this direction, most studies by now have involved cutting and chemical functionalization of CNTs, or attachment to polymers with solubilizing features. This approach has two disadvantages. On one hand, tedious chemical derivatization is often required, while on the other hand, these CNT derivatives may have significantly different properties than those of pristine

materials. CNTs can be dissolved in aniline without any prior chemical functionalization, and this material is then soluble in a variety of organic solvents, which represents the first observation of significant dissolution of pristine CNTs in standard organic solvents. For future work involving the separation, purification, and chemical functionalization of CNTs, solubilized nanotubes have a distinct advantage. For example, one can envisage CNT-aniline solutions for the formation of nanocomposites or thin films, which would solve some of the practical problems involved in making nanotube-based electronic and field emission display devices [60]. The strong fluorescence emission of CNTs should also be a useful probe to illustration of the physical and biological properties of these materials.
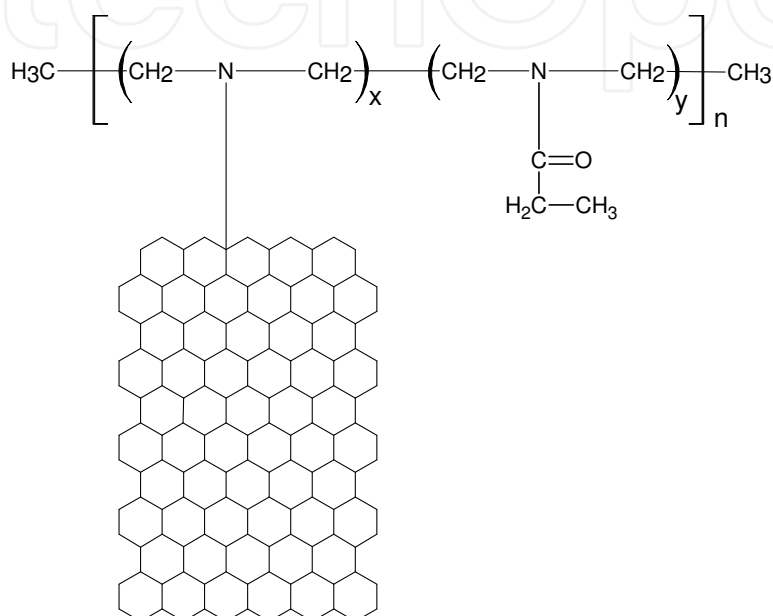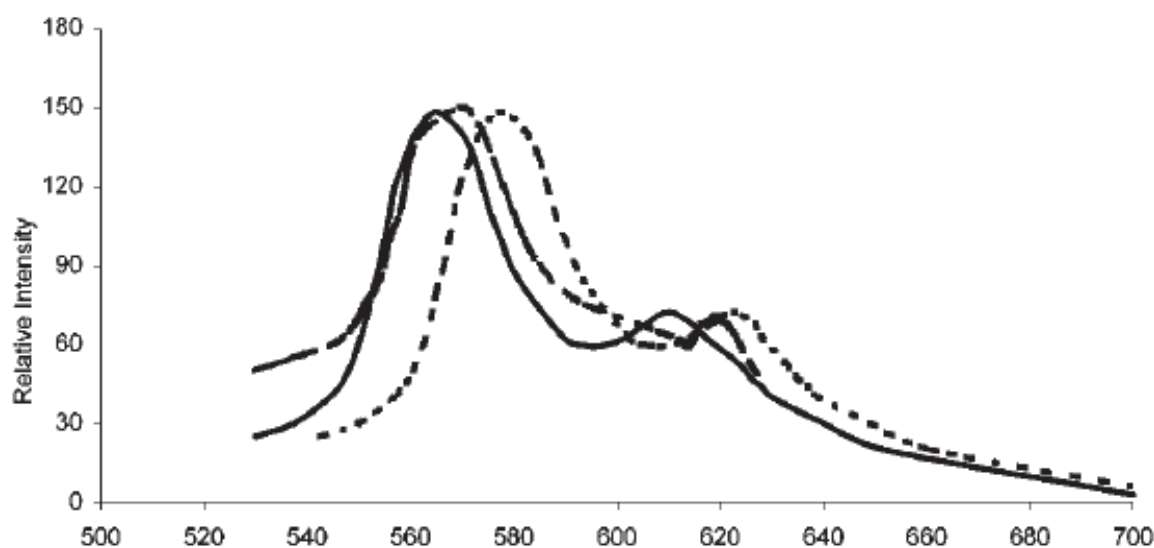

Fig. 21. Idealization of the PPEI-EI attachment [59]

Fig. 22. Emission spectra of aniline dissolved carbon nanotubes in different solvents: in acetone (—), in toluene (- · -), and in methanol (---). All samples were excited at 500 nm [61].

Strong fluorescence can be observed upon exciting the diluted SWNT-aniline solutions at 500 nm. Figure 22 shows the emission spectra of solutions in acetone, toluene, and methanol, respectively. The maximum emission in acetone is observed at 565 nm with a shoulder at 610 nm. In methanol, the emission is redshifted by 20 nm without any change in intensity. The shift of the emission maximum in polar/nonpolar solvents is unanimous with charge separation in the excited state. The quantum yield of fluorescence of SWNT-aniline in acetone is 0.30, considerably higher than that of aromatic molecules. Luminescence has been observed at slightly longer wavelengths for polymer-bound CNTs but it is controversial for the origin of this fluorescence. The quantum yields for CNT-aniline solutions are higher than those for the polymer-bound CNTs as well. Precautions are taken to prevent interference from fluorescence of small aromatic species and other impurities.

Composites of polymers and CNTs have been studied as materials not only for mechanical reinforcement but also for optoelectronic devices such as polymer light-emitting diodes (LEDs) and photovoltaic cells. Curran et al. reported 5 times better thermal stability from the composites LED's of PmPV and MWNTs [62]. Ago et al. fabricated photovoltaic devices using a heterojunction of PPV and MWNTs, and obtained about twice the external quantum efficiency compared to the standard indium-tin oxide (ITO) based devices [63].

The spectral-resolved photoluminescence of pure polymers and composites has been studied [64]. While the photoluminescence intensity of m-PMEH-PPV increases with temperature, composites slightly varies without order.
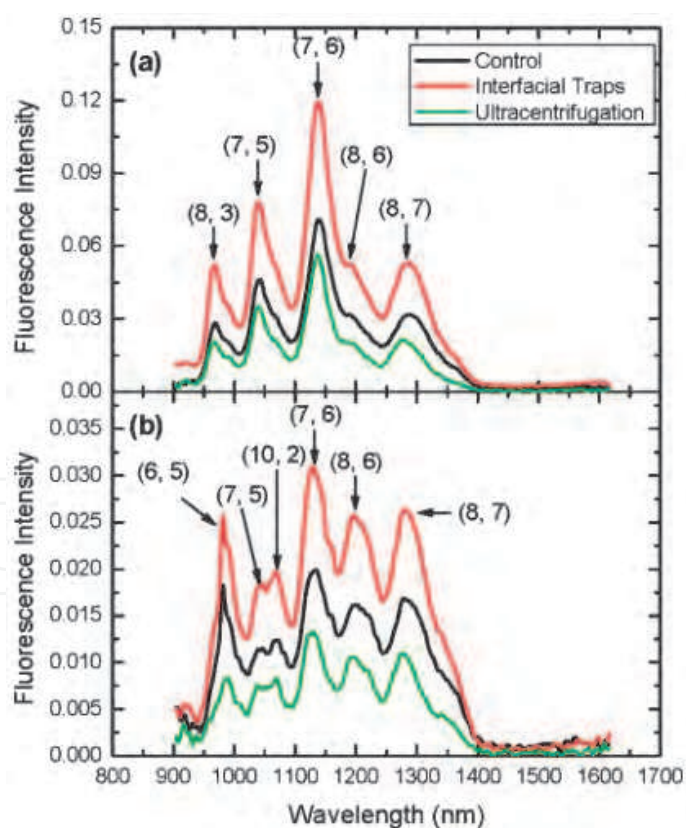

Fig. 23. Fluorescence spectra of Gum Arabic-suspended SWNTs from an initial mass concentration of 0.03 mg/mL of raw material with (a) excitation at 662 nm, and (b) excitation at 784 nm [66]. The control spectra were the samples after homogenization and sonication. This sample was then subjected to either ultracentrifugation or interfacial traps.

The conventional method to disperse individual nanotubes in aqueous solutions is by high-shear homogenization and ultrasonication in various surfactant solutions. While individual nanotubes are coated with a surfactant, some SWNT bundles remain because of large van der Waals attractions [65]. The bundling of nanotubes perturbs the electronic structure quenching the fluorescence of SWNTs. Ultracentrifugation is often used to remove nanotube bundles, but it is limited to analytical scales. Therefore, alternative routes are needed for large-scale removal of SWNT bondles.

R. K. Wang et al. introduced a process to remove nanotube bundles from aqueous suspensions by liquid-liquid interfacial trapping at toluene-water interfaces [66]. The approach is simpler than ultracentrifugation, and its resultant suspensions also have higher fluorescence intensities reflecting a higher concentration of individually suspended nanotubes. Fluorescence spectra of the aqueous phase were recorded with excitation at 662 and 784 nm, shown respectively in Figure 23a and 23b. In order to make a comparison, the spectra after homogenization and ultrasonication was shown as well as the spectra using traditional ultracentrifugation rather than interfacial trapping. The spectra showed that ultracentrifugation results in an obvious decrease in fluorescence intensity, indicating the removal of individual nanotubes.

5. Metal-contained emission systems of modified CNTs

It is an arising hot point that makes the metals cooperate with the CNTs by a certain kind of physical or chemical bonds, froming composites completely new. A large number of metals have been taken into consideration raging from the metals we could see everyday to rare-earth metals as well as the noble ones like Au and Ag. By cooperating with metals, we could obtain the modified CNTs with amazing new functions.

5.1 Lanthanide complexes as emission centers

Rare earth elements are of great importance in magnetic, electronic, and optical materials because of the number of unpaired electrons in their shells [67]. The novel properties of rare earth compounds make them rather appealing for practical applications in, for example, luminescence, catalysis, florescence imaging, and biological fields [68].

At the same time, more and more researchers have focused on the coating of CNTs. Because coating CNTs exhibit better physical and chemical properties and will lead to an even more diverse range of applications. For these reasons, the coating of CNTs with lanthanide related compounds is beginning to emerge.

Chinese researchers reported for the first time that rare earth fluoride EuF_3 and TbF_3 nanoparticles could be in situ bound to MWNTs through a simple and efficient synthetic route without causing a significant modification of the energy states of the MWNTs [69] [Figure 24].

MWNTs with an average outer diameter between 20 and 50 nm and length up to a dozen micrometers were prepared by the thermal catalytic decomposition of hydrocarbon [70] and the purity was over 90%. First, the MWNTs were dispersed in a 1 wt% sodium dodecyl sulfate (SDS) aqueous solution to modify the MWNTs surface by ultrasonication for 4h. After further washing and drying, 100 mg SDS adsorbed MWNTs was sonicated in 20 ml 0.1 mol/L $Ln(NO_3)_3$ (Ln = Eu^{3+}, Tb^{3+}) solution for 5 min, then 20 ml 0.3 mol/L NaF solution were slowly added into the mixture above with vigorous stirring. After 24 h reaction, the final products were washed repeatedly with water and then dried for 12 h at 100℃ [69]. EuF_3

and TbF_3 nanoparticles with size of less than 10 nm were coated on MWNTs successfully by a simple and effective in situ synthetic method without severely changing the energy states of the MWNTs. This method could also be extended to other transition metal and rare earth elements compound nanostructures. It should be further noted that this new type of hybrid CNTs with coated rare earth fluoride nanoparticles on the sidewall may have more interesting potential applications in field emitters and nanometer-scale optoelectronic devices.
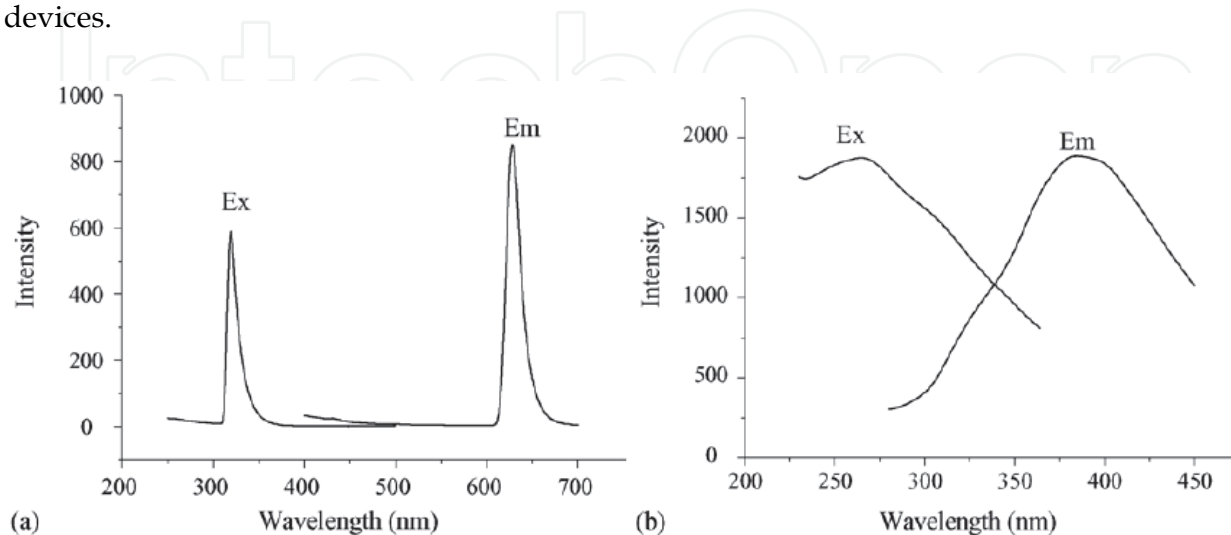

Fig. 24. Excitation and emission spectra of (a) EuF_3/MWNTs and (b) TbF_3/MWNTs [69]

As it is well accepted, the surface of a nanotube is often not ideal for coating; therefore the nanotubes have to be treated before coating. Previous reports have demonstrated that boilling the CNTs with oxidizing acids was an effective way for coating CNTs with CeO_2, while the CNTS are dispersed into nitric acid and heated at 500℃ for 2 h in air, only few CeO_2 particles absorbed on CNTs[71].

CNTs coating with europium oxide by a simple method is first reported by Chinese scientists [72]. Researchers covered the CNTs with a uniform layer of Eu_2O_3. Such kinds of CNTs have the potential applications in the field of emission display materials and luminescent materials. At the same time, europium oxide nanowires may be prepared by using CNTs as removable templates.

Coated CNTs are prepared as follows: CNTs were produced by catalysis and dissociation of hydrocarbon compounds as original material at high temperature. The average diameter of CNTs is found to be about 20 nm by TEM. The CNTs were suspended in a solution of concentrate nitric acid containing europium nitrate and refluxed for 4.5 hours [73]. When the mixture was cooled to room temperature, the ammonia solution with a concentration of 2.5wt% was added dropwise until the pH value reaches 9[74].Then the mixture was filtered and annealed in a stream of N_2, at 700℃ for 2 hours. After the Sample was washed with distilled water, the solvent was removed and the samples were dried for 5 hours at 100℃.

Another investigation had been presented by Chinese scientists on the luminescence of MWNTs with carboxylic groups [MWNT (-COOH)] and the Eu (III)/MWNT (-COOH)$_n$ composite [75].

MWNTs were prepared and purified as follows[76].In a pipe face, with reagent based on Ni and ethylene gas, raw MWNTs were eliminated with acid, 20% hydrofluoric acid and

hydrochloric respectively. MWNTs which were larger than 98% purity were obtained. Then, the purified MWNTs were suspended in concentrated nitric acid and refluxed for 48 h. The mixture was to be filtered and washed with deionized water repeatedly until the pH value approached 7. After drying, MWNT (-COOH) $_n$ was obtained.

MWNT(-COOH)$_n$ was suspended in ethanol and refluxed for 2 h, then the europium(III) chloride solution in ethanol was slowly dripped into suspension. The pH value of mixture dropped to 3 from 7 gradually in half an hour. Triethylamine was then added to keep the pH value at about 6. The mixture was filtered and washed with ethanol 24 h later until the pH value reached 7. Having been dried, the Eu(III)/MWNTs(-COOH)$_n$ composite was obtained[75].

Both MWNT (-COOH) $_n$ and the Eu^{3+}/MWNT (-COOH) $_n$ composite demonstrated luminescence, while the luminescence from the composite was stronger than that from MWNT (-COOH) $_n$, and the luminescence peak position of the composite slightly red-shifted to a longer wavelength [Figure 25]. The difference could be attributed to the coordination of Eu^{3+} with carboxylic groups on MWNT (-COOH) $_n$. The above results may have potential use in optoelectronic devices.
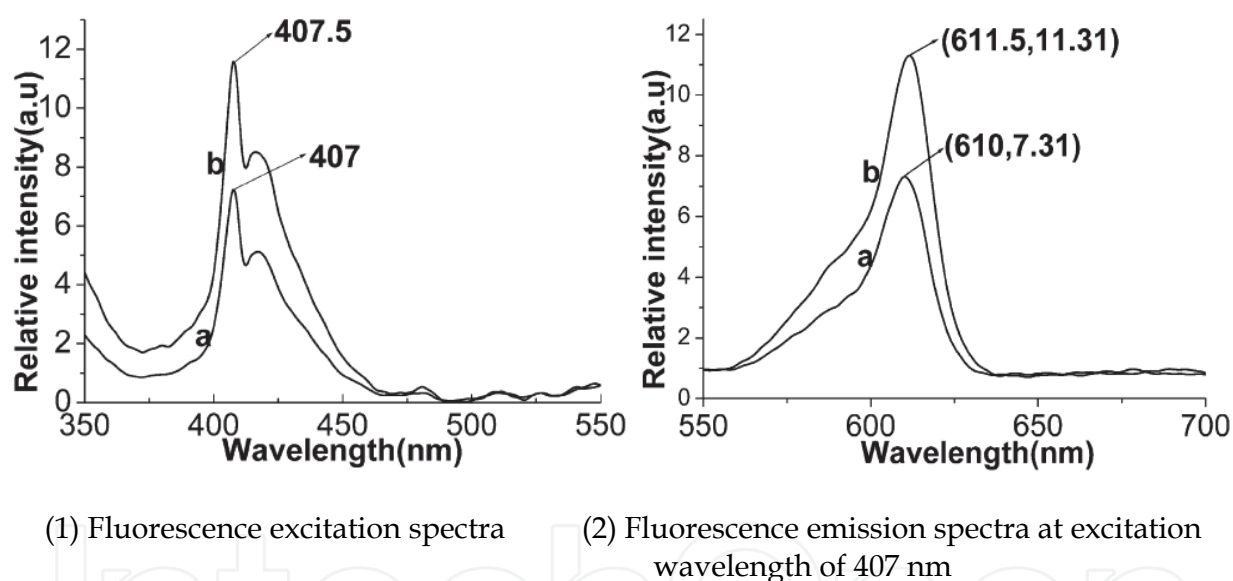

(1) Fluorescence excitation spectra   (2) Fluorescence emission spectra at excitation wavelength of 407 nm

Fig. 25. Excitation and fluorescence characteristics of (a) MWNT (-COOH) $_n$ and (b) Eu^{3+}/MWNT (-COOH) $_n$ composite [75]

J. G. Tang and his fellows once worked on the nanoblock building strategy to obtain hybrid fluorescent nanoblocks through grafting ligand–antenna integration oligomer onto nanoscaffolds [77] [Figure 26]. In their research, CNTs were studied as nanoscaffolds to anchor organic oligomers and further to complex with lanthanide (i.e. Tb^{3+}) acceptor to obtain hybrid fluorescent nanoblocks. These built hybrid nanoblocks showed sharp fluorescent emission under ultraviolet excitation [Figure 27]. These results presented an important method to prepare small ligands from nanoscaled scaffolds, and generated the excellent fluorescent hybrid nano blocks, in which CNTs provided stable structural hosts for lanthanide complexes. Through the D-A(Donor-Acceptor) strategy of getting fluorescent nanoblocks, the promising nanohybrid luminescent materials will be emerged.
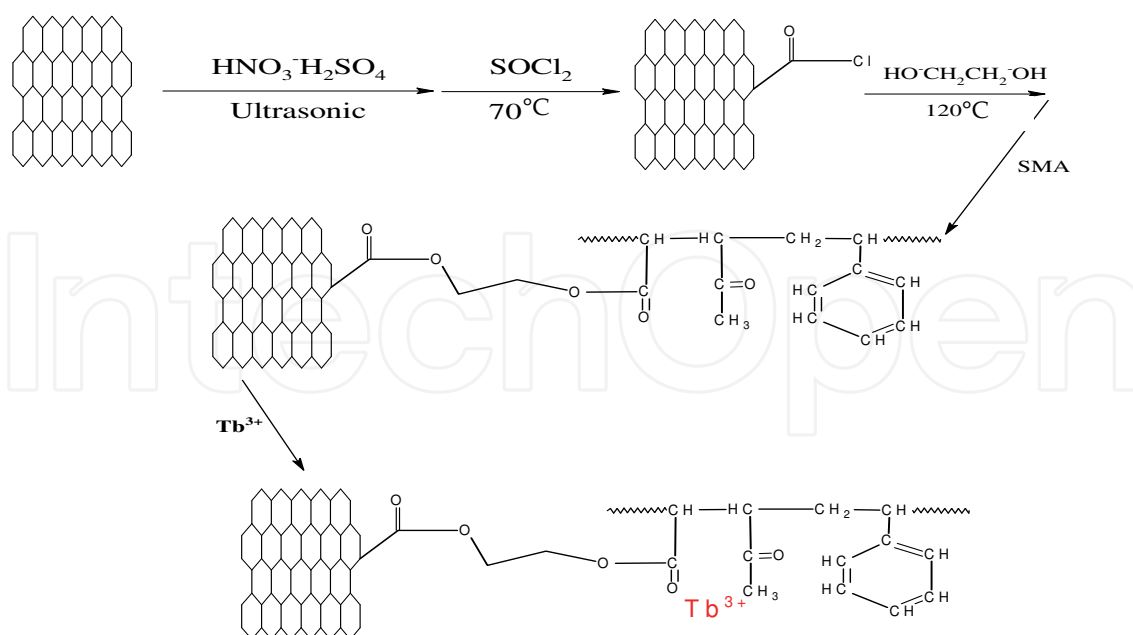
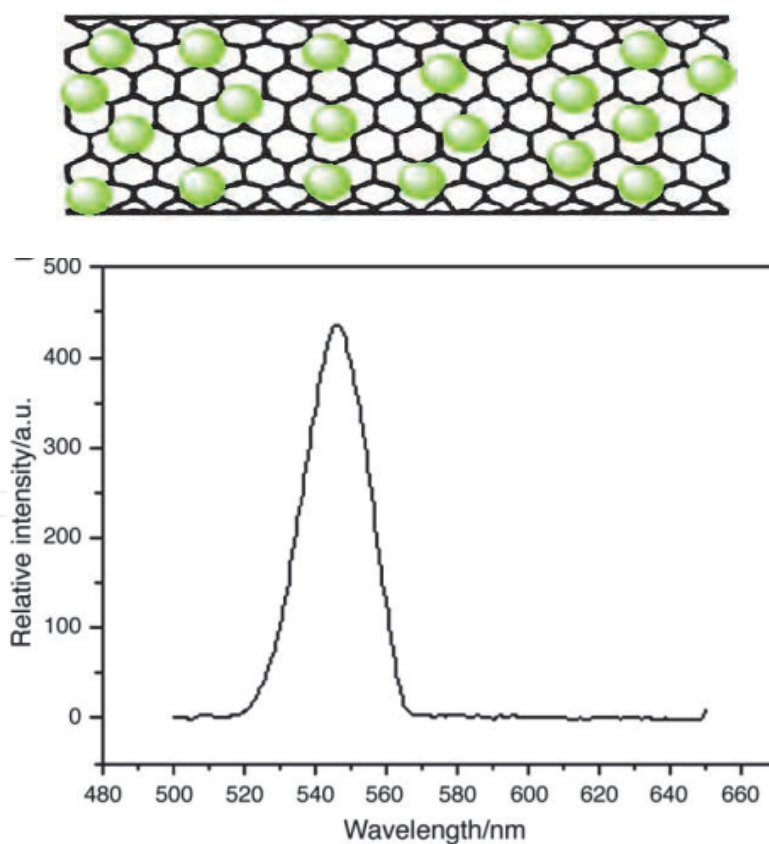Fig. 26. Steps of preparing fluorescent nanoblock of carbon nanotube [77].

Fig. 27. The sketched images of fluorescent nanoblocks and Emission spectrum of fluorescent nanoblocks of LSMA-CNTs (LSMA-CNTs were excited by ultraviolet radiation: The excitation peak at 270 nm is a symmetric narrow band ranging from about 260–280 nm.)[77].

5.2 Noble metal nanoparticle-existed systems

A novel stragety to attach gold nanoparticles to CNTs selectively has been developed [78]. Just as Figure 28 shows, the MWNTs were firstly chemically modified with an H_2SO_4-HNO_3 treatment, and then were suspended in a concentrated sulfuric acid/nitric acid mixture (3:1 in volume) and sonicated in a sonic bath for 2 h. A CNT mat was obtained after filtration and was then thoroughly washed with a dilute sodium hydroxide aqueous solution.
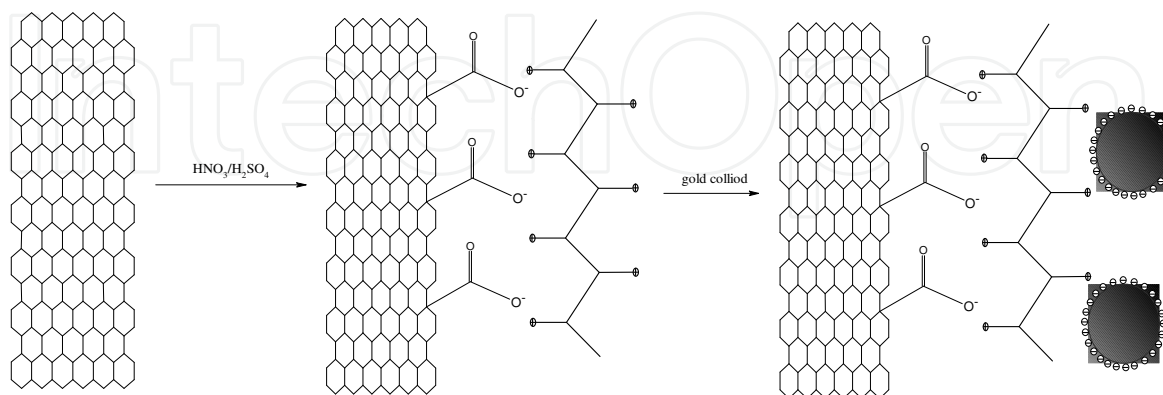

Fig. 28. Attachment of gold nanoparticles onto CNTs [78]

The nanotube suspension was then mixed with a cationic polyelectrolyte, poly (diallyldimethylammonium) chloride (M_w≈100,000-200,000), and NaCl aqueous solution for 30 min. PDADMAC was adsorbed to the surface of the nanotubes because of the electrostatic interaction between the carboxyl groups and the polyelectrolyte. After filtration and thorough washing with a NaCl aqueous solution and deionized water, the nanotubes were dispersed in water again, and mixed with a gold colloid (10 nm) for 30 min. The negatively charged gold nanoparticles were anchored to the surface of the nanotubes through the electrostatic interaction between the polyelectrolyte and the nanoparticles.

By choosing different kinds of polyelectrolytes, the surfaces of CNTs can be tailored to be negatively or positively charged, so many other nanoparticles (such as magnetic nanoparticles, semiconductor nanocrystals) can be selectively attached to the surfaces of nanotubes [Figure 29]. Additionally, this method of decorating nanotubes can be used to identify the location of functional groups. These nanoparticle-decorated nanotube heterostructures could be used in catalytic, electronic, optical, and magnetic applications [79].
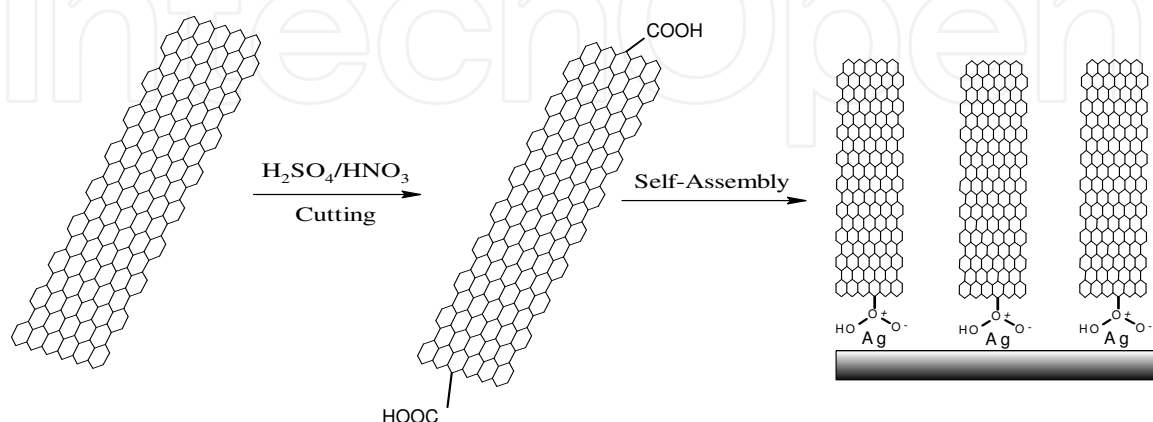

Fig. 29. Chemical alignments of oxidative CNTs on silver surface [79]

Another method has been reported for immobilizing the randomly tangled SWNTs on silver surface, forming an organizing nanotube assembly. The long and randomly tangled SWNTs which have already been prepared are cut into short pipes by chemical oxidation, which produced carboxyl groups at the open end of the tubes [80]. Basing on the fact that spontaneous adsorption of long chain *n*-alkanoic acids can occur via the carboxyl groups on various metal native-oxide surfaces [81, 82, and 83], such oxidatively shortened SWNTs would be immobilized on the silver surface.

H. J. Dai et al. first report on metal enhanced fluorescence of surfactant-coated carbon nanotubes on nanostructured gold substrates [84]. The photoluminescence quantum yield of SWNTs is observed to be enhanced more than 10-fold. It is suggested that the mechanism of SWNT fluorescence enhancement is due to radiative lifetime shortening of the excited state, resulting from resonant coupling of nanotube emission with the scattering and reradiating component of plasmons localized on the surface of the metal substrate.

6. Applications of fluorescent CNT

Due to the unique properties on photology, electromagnetism and chemistry, the modfied CNTs with fluorescent property have already been widely used as production materials of optical devices, electrical equipment and biomedicine kits. The excellent performance of them amazes us greatly. Now we will give a brief introduction to the most important and representative three of all these applications. They are, respectively, OLEDs, solar cells and biosensors.

6.1 OLEDs

CNT thin films now have had amazing applications. Their outstanding optical property as well as electrical behaviors makes them the perfect choice for the OLED materials. There has been a considerable interest to find a new material as the replacement of the traditional materials. On one hand, the traditional indium tin oxide (ITO) anodes are so brittle that they are easy to crack. On the other hand, indium is rare-earth metal, whose supply is lacked. Thus, due to their flexibility and work function (4.7eV-5.2eV) [85, 86], as well as the chemical stability during the wet processing of OLEDs, the CNT thin film-made OLED anodes are now more attractive.

E. C-W Ou and co-workers treat the surface of CNT thin films with nitric acid, PEDOT: PSS and CNT composition (PS^c) and polymer coating, and further study the influence of these treatments on the properties of OLED devices [87]. The result is gratifying-the modification of CNTs will benefit the enhancement of properties of these devices, making people full of confidence to the future of OLEDs.

6.2 Solar cells

As a completely new resource of renewable energy and a potential kind of alternatives of traditional inorganic solar cells, organic photovoltaic solar cells start to attract more and more attentions from researchers all around the world as well as the interest to study on them. The processing of these new organic photovoltaic solar cells is relatively simple. They are made from inexpensive organic materials, making the production on a large scale possible.

There are several reasons for using modified CNTs in this kind of materials. The big surface area of the CNTs sets a good stage for the morphological construction. Also, the high aspect

ratio allows the settlement of percolation at relatively low doping levels, which provides the way to high carrier mobility and efficient charge transfer of certain electrodes. The conducting polymer nanocomposites, such as SWNT-epoxy composites, whose percolation thresholds are extremely low, have already been developed.

Recently, Brazilian scientists [88] announced that the open-circuit voltage was raised to 1.8V by the use of modified CNTs combined with polarized polybithiophene layers, resulting in a conversion of 1.5% [89]. Generally, the CNTs stack into bundles in polymers by the interaction of Van der Waals force with each other. Thus, the thiophene groups located at the edges and defects of the CNTs will improve the dispersion of CNTs in conducting polymer, as well as the compatibility of them. All of these will of course increase the efficiency of polymer/CNTs solar cells.

Maurizio Prato et al. carried their research on the phthalocyanine-pyrene conjugates, ZnPc-Py and H_2Pc-Py, which had emerged as valuable building blocks for assembling electron donor-acceptor hybrids with SWNTs [90]. Owing to the strong ability of pyrene to adhere to SWNT sidewalls by means of π-π interactions, they had exploited this polyaromatic anchor to immobilize metal-free (H_2Pc) as well as zinc (ZnPc) phthalocyanines onto the surface of SWNTs. Encouraged by the charge-transfer features, researchers have utilized ZnPc/SWNT and H_2Pc/SWNT thin films in photoelectrochemical cells to test their solar energy conversion potential. Performances have been realized that are much superior to those of previously reported SWNT conjugates and hybrids [91].

6.3 Biosensors

Due to the weak fluorescence of CNTs [6, 92], a large number of efforts have been invested in developing the fluorescent CNTs by means of covalent or noncovalent modification [93, 94]. Thus, the fluorescent molecules such as pyrene and porphyrin are often used for modification of CNTs. However, most of the organic compounds have a short fluorescence lifetime, which is easy to quench at the same time.

As is known to all of us that the rare-earth compounds are often used to manufacture laser materials, optoelectronic devices and fluorescence probes [95, 96]. Chinese scientists designed and synthesized the SWNTs covalently modified by europium (Eu^{3+}) complex [97] [Figure 30]. The modified SWNTs can emit strong red luminescence upon excitation. Meanwhile, the research on the luminescence change of modified SWNTs after being bonded to DNA was also studied.
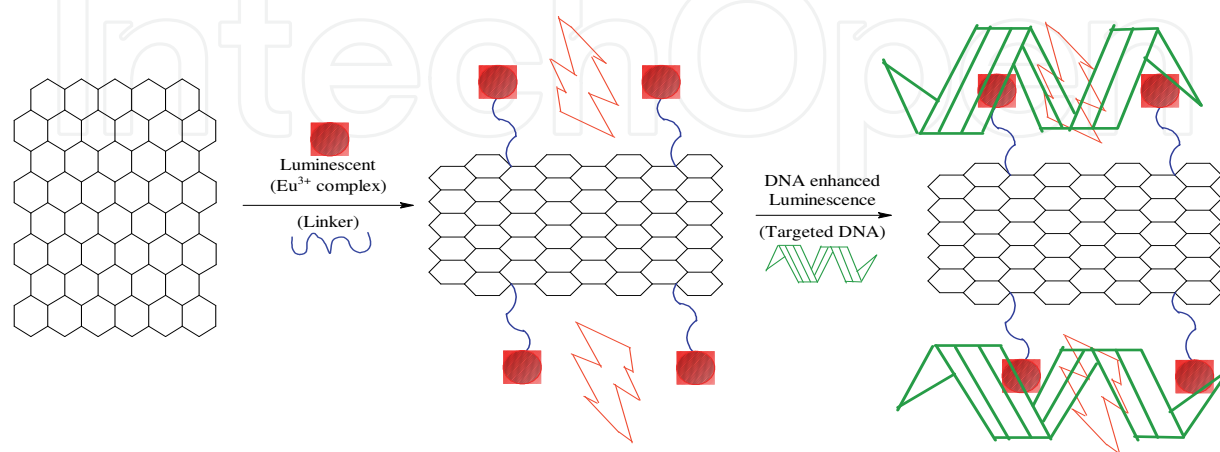

Fig. 30. Schematic representation of the luminescent Eu^{3+}-Complex covalently-modified SWNT and its luminescence enhanced by DNA [97]

Making the use of these unique properties, we can manufacture biosensors and many other devices with these modified CNTs. Another effective and novel self-assembled oligonucleotide/SWNT composite has been reported by Yang and co-workers [98]. This kind of composites are able to judge the sequence of certain DNA by the use of a self-assembled quenched complex of fluorescent Single-stranded DNA(ssDNA) and SWNTs as an efficient molecular beacons which can fluorescently detect single nucleotide differences in DNA in homogeneous solutions. In this way, the application of CNTs in biosensors will be broadened greatly.

7. Conclusions and future remarks

In summary, in this chapter, we focus mainly on the recent advances and achievements on the design and functionalization of CNTs, including noncovalent and covalent modification, polymer-existed system and metal-contained system, for the purpose to obtain enhanced fluorescence property, as well as properties on many other sides. As demonstrated by these remarkable examples, the relationship between the structures of modified CNTs and the fluorescence property helps to offer new attractive prospects for constructing CNT-based molecular optoelectronic and photon devices with desired functionalities. Many of these devices have already been used in practice or even industry, which push forward the development of our society and science, as well as profiting us a lot, both on economy and everyday life. However, there are still so many mechanisms and potentials waiting to be explored. For this reason, the research on the relationship between the structure of CNTs as well as their derivatives and properties of them is still one of the hottest and hopeful fields in nanotechnology.

Now, the production of CNTs has become cheaper and easier than before, which opens the door to more researchers. As the rapid development of nanotechnology, the overwhelming trend of the functionalization of CNTs has turned to the technological application of them. For the achievements we have already scored(only a small portion is listed in this review), there are sufficient reasons to hold an optimistic attitude towards the industrial products of CNTs in the near future, as well as the going-on researches in laboratories.
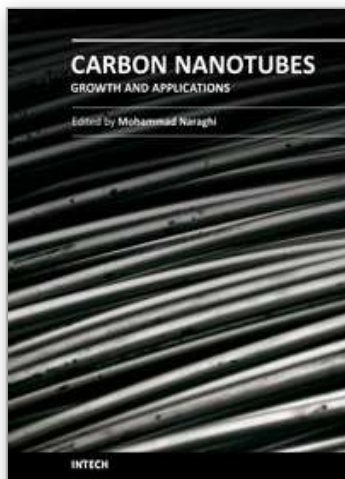
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Edited by Dr. Mohammad Naraghi

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