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Fabrication and Applications of Carbon Nanotube-Based Hybrid Nanomaterials by Means of Non-Covalently Functionalized Carbon Nanotubes

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1. Introduction

Carbon nanotubes (CNTs) including single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) are allotropes of carbon with cylindrical nanostructures. These cylindrical carbon molecules exhibit many fascinating properties including high aspect ratio and tubular geometry, which provides ready gas access to a large specific surface area and percolation at very low volume fractions. They also possess extraordinary mechanical, thermal, electrical and optical properties, which support CNTs as ideal building blocks in hybrid materials with potentially useful in many applications in nanotechnology, electronics and optics [Capek, 2009]. By templating against CNTs, a variety of functional components, such as metal nanoparticles (NPs), quantum dots, inorganic oxides and organic species, can be used to decorate CNTs sidewalls or fill CNTs matrix, forming varied CNT-based hybrid nanomaterials [Eder, 2010]. These yielded hybrids generally exhibit synergistic properties, which greatly optimize the technological potentials of CNTs and enable them to be applied in more versatile areas. However, CNTs generally exist in the form of solid bundles, which are entangled together giving rise to a highly complex network. Together with the chemically inert surfaces, pristine CNTs tend to lack of solubility and be difficult manipulated in any solvents, which have imposed great limitations to the use of CNTs as templates to assemble diverse functional components. Therefore, to efficiently fabricate CNT-based nanohybrids, it is necessary to activate the graphitic surfaces of CNTs. In this direction, two types of CNT-surface-functionalization strategies, covalent and non-covalent methodologies, have been extensively explored in the recent decades.

The end caps of CNTs (when not closed by the catalyst particles) tend to be composed of highly curved fullerene-like hemispheres, which are therefore highly reactive, as compared with the sidewalls [Niyogi et al., 2002]. The sidewalls themselves contain defective sites such as pentagon-heptagon pairs called Stone-Wales defects, sp^3 -hybridized defects and vacancies in the nanotube lattice [Hirsch, 2002]. These intrinsic defects provide versatile alternatives to covalently modify the CNTs by means of varied organic chemistry. For instance, Tessonnier et al. [Tessonnier et al., 2009] recently explored to functionalize

MWCNTs with amino groups by deprotonation-carbometalation and subsequent electrophilic attack of bromotriethylamine. Sidewall functionalization also can be achieved by ozonolysis of CNTs followed by treatment with varied reagents [Banerjee & Wong, 2002]. Dissolved lithium metal in liquid ammonia was also used to hydrogenate SWCNTs [Pekker et al., 2001]. In addition, free radicals generated by decomposition of organic peroxide in the presence of alkyl iodides have been used to modify small-diameter SWCNTs [Peng et al., 2003]. More recently, we have developed a rapid, facile and green strategy to modify the pristine CNTs with hydroxyl groups by means of plasma treatment technique [Li et al., 2009]. Note that this surface-modification method effectively avoids the use of any toxic organic solvents or additional surfactants, which not only lowers the production cost but also simplifies the preparation procedures. Although these pioneering methodologies have been extensively explored, the traditional oxidation strategy is still the most common and efficient route to functionalize CNTs so far. In such sidewall modification process, the intrinsic defects of CNTs are supplemented by oxidative damage to the nanotube framework by strong acids which leave holes functionalized with oxygenate functional groups such as carboxylic acid, ketone, alcohol, and ester groups [Chen et al., 1998]. In particular, the treatment of CNTs with strong acids such as nitric acid or with other strong oxidizing agents including $\text{KMnO}_4/\text{H}_2\text{SO}_4$, oxygen gas, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ and OsO_4 [Banerjee, et al., 2005], tends to open these tubes and to subsequently generate oxygenated functional moieties that serve to tether many different types of chemical functionalities, such as polymers, inorganic oxides, and metal nanoparticles, onto the ends and defect sites of CNTs, yielding a wide range of CNT-based nanohybrids with extensive applications.

For example, Salavagione et al. [Salavagione et al., 2010] directly grafted poly(vinyl chloride) onto the carboxylic groups modified MWCNT surfaces through esterification reactions in an efficient “grafting to” method. Pei et al. [Pei et al., 2007] successfully grafted poly(2-hydroxyethyl methacrylate) (PHEMA) brushes to the MWCNTs surfaces by means of a surface-initiated reversible addition and fragmentation chain transfer (RAFT) polymerizations, yielding well dispersed CNT/polymer hybrid nanostructures. After hydrolysis of PHMA in the presence of HCl, poly(methacrylic acid) grafted MWCNTs were achieved and showed higher loading capacities for metal ions such as Ag^+ . Beside these, a variety of polymerization techniques, such as in-situ radical, anionic, emulsion, Ziegler-Natta and electrochemical polymerizations, have been extensively explored to surface-graft diverse polymer chains from covalently surface-modified CNTs [Tasis et al., 2006]. For the fabrication of CNT/inorganic oxide hybrid nanostructures, numerous studies have been involved. Bottini et al. [Bottini et al., 2005] explored to graft tetraethyl or tetramethyl-orthosilicate (TEOS or TMOS) onto carboxylic acid groups contained CNTs obtained under concentrated HNO_3 oxidizing conditions, forming coupling aninopropyltriethoxysiane functionalized CNTs through a carboxamide bond. On the basis of these surface-modified CNTs, silica beads were generated and decorated along the CNTs by a sol-gel process in the presence of ammonia water. More recently, Zhang et al. [Zhang et al., 2009] explored a facile route to assemble 3-(trimethoxysilyl)-1-propanethiol modified silica nanoparticles onto the sidewalls of oxygenated moieties contained MWCNTs in the presence of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide), resulting in the formation of nonionic nanofluid hybrid materials. In addition, the suitable surface modification of CNTs also provide promising substrates for the deposition of varied noble metal NPs. As a typical example, Gu et al. [Gu et al., 2009] further modified oxygenated MWCNTs with imidazole salts motifs whose counterions allow to be exchanged with metallic ions. Upon reduction

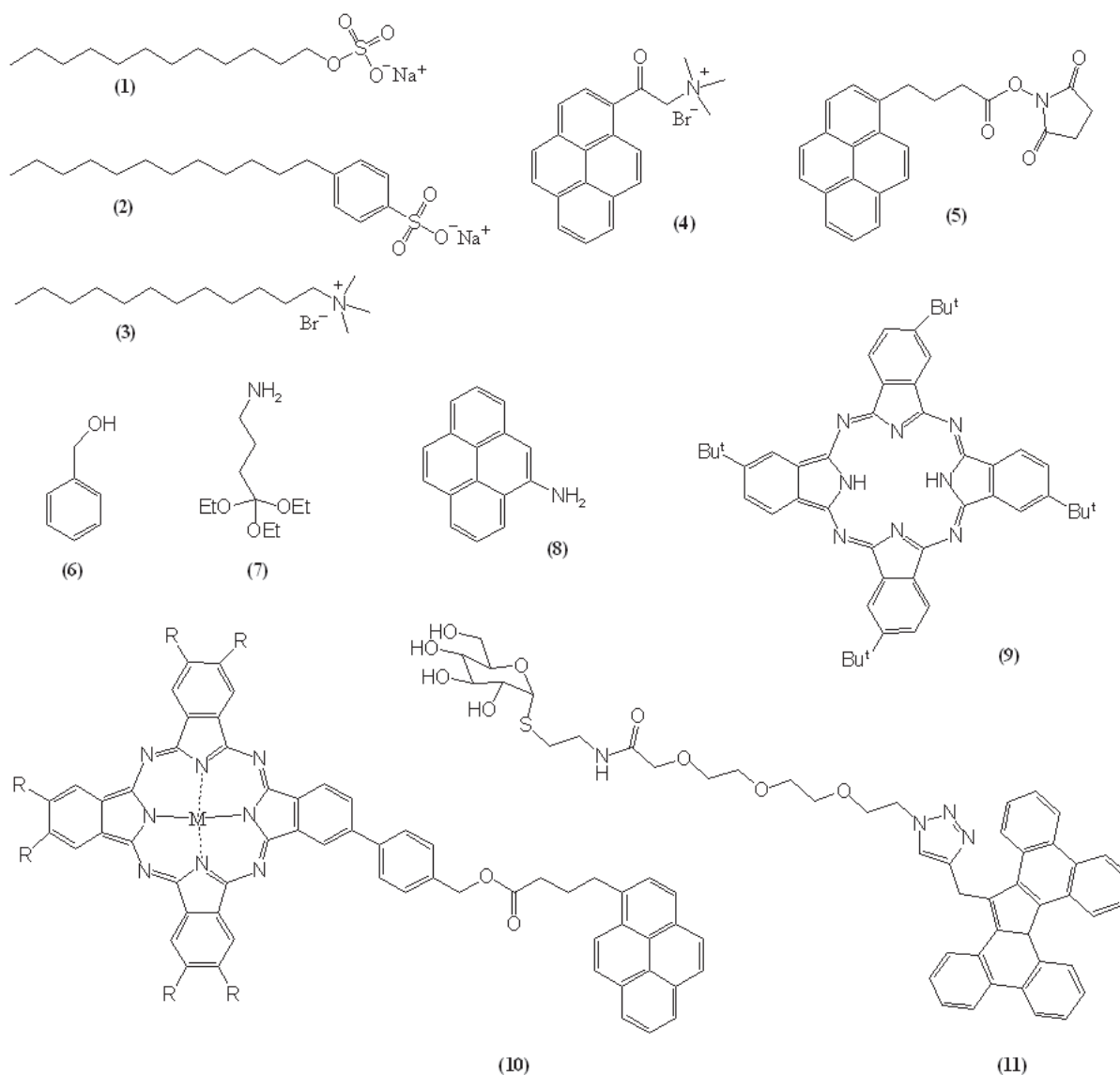
reactions, those metal ions are in-situ transformed to metal NPs, yielding CNT/metal nanostructures with good electrochemical properties. Han et al. [Han et al., 2004] demonstrated a simple and effective alternative to assemble monolayer-capped metal NPs onto the CNT surfaces via a combination of hydrophobic and hydrogen-bonding interactions between the capping/mediating shell of metal NPs and CNT sidewalls. The loading and distribution of NPs on CNT sidewalls can be well-controlled depending on the relative concentration of metal NPs, CNTs and mediating or linking agents. As another representative example, we recently explored an effective protocol to fabricate CNT-based nanohybrids, in which hydroxyl groups were introduced onto the sidewalls of pristine SWCNTs by means of plasma treatment technique.[Li et al., 2009] Followed by a co-condensation process between those hydroxyl groups bearing on the SWCNTs and TEOS (or together with MPTO), a uniform SiO_2 and thiol groups-functionalized SiO_2 coating on the CNTs can be fabricated effectively. By means of $\text{SWCNT@SiO}_2\text{-SH}$, a stable $\text{SWCNT@SiO}_2/\text{Ag}$ heterogeneous hybrid has been generated via in-situ growth process in the absence of any additional reducing agents.

Although the conventional covalent CNT-surface-modification methodologies such as strong oxidizing acids treatments can introduce a variety of organic groups on the CNTs surfaces which can serve as effective media to tether or immobilize varied functional components to produce versatile hybrid nanostructures, those introduced functional groups tend to be with limited control over their number, type and location. Moreover, such treatment processes generally cause the surface etching and shortening of CNTs, resulting in the compromise of the electronic and mechanical properties thus suppress their extensive applications. In addition, the deposition of functional components on such covalently surface-modified CNTs often leads to the non-uniform coatings owing to the non-uniform functionalities on the such modified CNT surfaces. Therefore, to achieve uniform coatings on CNTs sidewalls, recently developed non-covalent (non-destructive) methods have provided more facile and efficient alternatives to homogeneously functionalize CNT sidewalls by means of van der Waals interactions, hydrogen bonding, π - π stacking, or electrostatic interactions in the presence of CNT-surface-modifiers such as small molecular surfactants and polymers. In those non-covalently functionalization processes, CNT-surface-modifiers play key roles which not only endow the CNTs with certain dispersity in solvents, but also act as “bridges” to integrate various of functional components onto the CNT surfaces to generate varied CNT-based nanohybrids. Moreover, such resultant hybrids generally exhibit synergistic properties while still reserving nearly all the intrinsic properties of CNTs.

In the recent years, a variety of CNT-surface-modifiers have been developed and utilized to non-covalently functionalize CNTs to create versatile CNT-based hybrid nanomaterials targeted to specific applications (Scheme 1). In this chapter, the recent advances in the use of those non-covalent surface-modifiers for the fabrication of CNT-based hybrid nanomaterials are overviewed.

2. Small molecular CNT-surface-modifiers

To date, many small molecular CNT-surface-modifiers such as some amphiphilic molecules (surfactants) including ionic surfactants and aromatic compounds have been widely utilized to non-covalently functionalize CNTs surfaces (see Scheme 1). In the case of



Scheme 1. Different types of small molecular CNT-surface-modifiers.

small molecular surfactants, their hydrophobic parts tend to be adsorbed onto the CNT surfaces by means of diverse hydrophobic interactions, while the hydrophilic parts point towards and interact with the surrounding media. Those non-covalent interactions can effectively solubilise CNTs in certain solvents and prevent them from the aggregation into bundles and ropes. Moreover, those hydrophilic parts provide platforms for the integration of functional components onto the CNT sidewalls to achieve diverse hybrid nanostructures.

2.1 Ionic surfactants

For the ionic small molecular CNT-surface-modifiers, anionic sodium dodecylsulfate (SDS) surfactant has received the most enormous studies. It has found SDS arranged into rolled-up half-cylinders with the alkyl-groups of each molecule pointed towards the MWCNTs [Richard et al., 2003]. Such striation patterns on the sidewalls of MWCNTs were related to the presence of the long alkyl chains and are unaffected by the nature of hydrophilic groups.

It also believed that the simple alkyl chains of surfactants such as SDS, sodium dodecyl sulfonate (SDSA), dodecyltrimethylammonium bromide (DTAB) formed non-specific hydrophobic interactions with CNTs, which result in the loose packing of surfactant molecules around CNTs [O'Connell et al., 2002; Moore et al., 2003]. In addition, the length and shape of the alkyl chains of surfactants also play key roles for the efficiency of the interaction of such surfactants with CNTs: longer and more branched alkyl groups are better than linear and straight ones, respectively [Wenseleers et al., 2004; Islam et al., 2003].

On the basis of those surface-modified CNTs, varied CNT-based hybrid nanostructures have been fabricated. For instance, using SDS as non-covalent CNT-surface-modifiers not only greatly enhance the dispersion of CNTs in water but also provide negative charges to the CNT surfaces, which make SDS-modified CNTs very useful for mediating the attachment of metal NPs on their surfaces. Following this direction, gold NPs were successfully in-situ generated and attached onto the SDS-modified MWCNTs, forming heterogeneous nanostructures [Zhang et al., 2006]. In addition, those surface-charged SDS-modified MWCNTs can be easily layer-by-layer assembled onto the indium tin oxide-coated glass plates mediated by the oppositely charged polyelectrolyte. Similarly, Lee et al. [Lee et al., 2005] decorated in-situ synthesized Pt NPs onto the sidewalls of SDS-functionalized CNTs. The resulting CNT/Pt hybrids exhibited high activity towards the oxidation of methanol.

Whisitt et al. [Whisitt & Barron, 2003] evaluated different surfactants for their ability to facilitate the deposition of silica NPs onto SWCNT surfaces in the acid conditions. By using anionic SDS, silica NPs were deposited around the bundles of SWCNTs to form coated ropes, while the use of cationic DTAB enabled a significantly better deposition and debundling of SWCNTs so that individual nanotubes were coated. They proposed that this effect is the consequence of the pH stability of the SWCNT/surfactant interaction. Acidification of a SWCNT/SDS solution results in the immediate formation of SWCNT ropes, while the SWCNT/DTAB interaction is far less susceptible to the changes of pH. Based on the SDS-modified SWCNTs, an optically homogeneous SWCNT/silica gel has also been fabricated via a sol-gel process [Zamora-Ledezma et al., 2008]. The resultant gel displays a strong fluorescence signal in the NIR, thus it is good candidate for the development of new opto-electronic devices with extended possibilities of processing, especially into thin films.

Besides the CNT/metal NPs and CNT/oxides hybrids, CNT/polymer nanostructures also can be achieved by means of ionic-surfactant modified CNTs. For example, Yang et al. [Yang et al., 2006] used sodium dodecylbenzene sulfonate (SDBS) to exfoliate SWCNT bundles into individual nanotubes with good dispersity in aqueous media. It was found that SDBS-functionalized SWCNTs can adsorb acrylonitrile monomers on their surfaces. After a conventional in-situ radical polymerization and a subsequent hydrolysis reaction, poly(acrylic acid) (PAA) chains were grafted onto the SWCNT sidewalls, producing pH-responsive SWCNT/PAA hybrid with controlled solubility in water depending on pH.

2.2 Aromatic-group-contained molecules

In contrast to the alkyl-chain-contained surfactants, aromatic-group-contained molecules are capable of forming more specific and directional π - π stacking interactions with graphitic surfaces of CNTs. This fact has been evidenced by the comparing results between the use of

SDS and SDBS [Zhang et al., 2006]. It was demonstrated that the presence of phenyl ring made SDBS more effective for the solubilisation of CNTs than SDS although they possess the same length of alkyl chains. Therefore, aromatic-group-contained molecules have been widely utilized to surface-modify CNTs. A typical example involves the use of benzene alcohol to non-covalently functionalized CNTs have been well demonstrated by Eder et al. [Eder & Windle, 2008a, 2008b]. They have found that the π - π interactions of benzene ring enable this surfactant to be adsorbed onto the CNTs' sidewalls. Simultaneously, the hydrophilic hydroxyl groups bearing on the benzyl alcohol-modified CNTs provide effective platforms for the hydrolysis of the titanium precursor to yield CNT/titania hybrid nanostructures with quite uniform titania coatings. After removal of CNT cores from CNT/titania nanohybrids via calcination treatment, anatase and rutile titania nanotubes can be achieved. This work also showed that benzyl alcohol strongly affected the phase transition from anatase to rutile, providing very high specific surface areas.

Recent studies have shown that the surfactants containing polyaromatic components such as pyrene generally demonstrate more affinity for the CNT surfaces compared with the simple aromatic compounds, resulting in the formation of more stable CNT sols. So far the related researches have been under intense investigations. For example, Bogani et al. [Bogani et al., 2009] synthesized pyrene-functionalized single-molecule magnets (SMMs) and non-covalently bridged them onto the CNT sidewalls, generating the first CNT/SMMs hybrids in conditions compatible to the creation of electronic devices. This work paves a way to the construction of "double-dot" molecular spintronic devices, where a controlled number of nanomagnets are coupled to an electronic nanodevice, and to the observation of the magneto-Coulomb effect. As another typical example, Li et al. [Li et al., 2006] explored to use 1-aminopyrene to non-covalently modify MWCNT sidewalls. Those amino moieties-contained CNTs exhibited specific adsorption capacities towards different NP precursors via electrostatic interactions and/or preferential affinity under appropriate conditions (Fig. 1). Followed by in-situ reduction or sol-gel processes, a wide range of NPs such as Pt, CdS, and silica were in-situ formed and decorated onto the sidewalls of CNTs with high specificity and efficiency. In addition, inspired by the immobilization of biomolecules onto CNT surfaces in a reliable manner, a bifunctional molecule, 1-pyrenebutanoic acid succinimidyl ester was synthesized and applied to non-covalently functionalize SWCNT surfaces (compound 5 in Scheme 1) [Chen et al., 2001]. By means of nucleophilic attack reactions, various protein and biological molecules such as enzymes can be subsequently covalently attached onto the surface-modified CNTs with a high degree of control and specificity. These surface-modified SWCNTs also can immobilize varied NPs such as ferritin, streptavidin and Au NPs.

Heterocyclic porphyrins and their derivatives are another class of polyaromatic molecules with specific π - π interactions with CNTs. Tetrabutyl-substituted phthalocyanine can non-covalently adsorb on CNT surfaces, forming nano-sized clusters which presumably consist of aggregated phthalocyanine molecules [Wang et al., 2002]. It was also found the CNTs can fade the colour of phthalocyanine solution in chloroform depending on the relative weight of CNTs in the composites. More recently, a new type of pyrene (Py)-substituted phthalocyanines (Pcs) including ZnPc-Py and H₂Pc-Py (compound 10 in Scheme 1) were synthesized and utilized to non-covalently functionalize SWCNTs via π - π interactions between the pyrene groups and CNTs, forming stable electron donor-acceptor SWCNT/ZnPc-Py and SWCNT/H₂Pc-Py hybrids [Bartelmeß et al., 2010]. Encouraged by

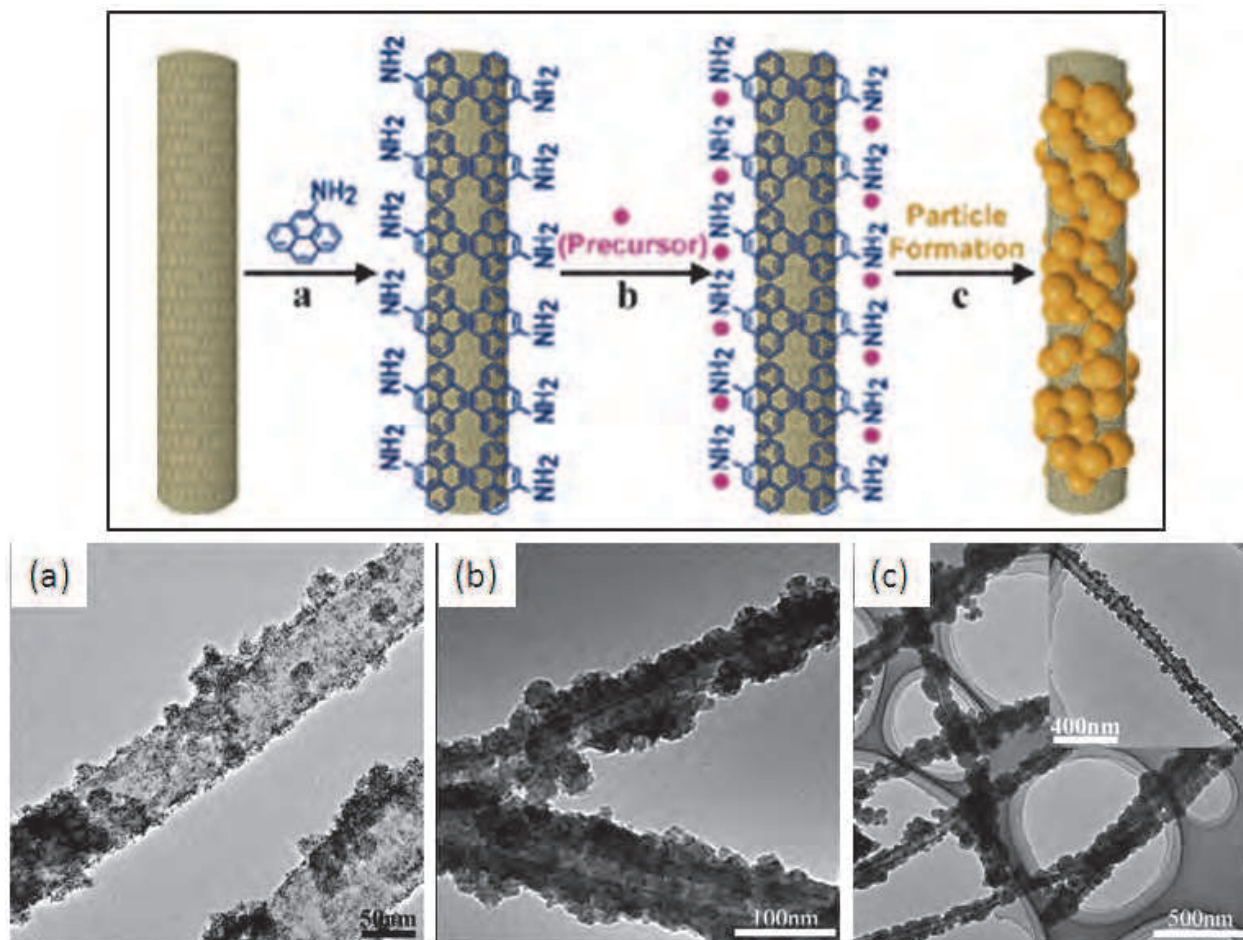


Fig. 1. (Top) scheme for the preparation of CNT/NPs hybrids on the basis of 1-aminopyrene-modified CNTs; (bottom) TEM images of (a) CNT/Pt NPs, (b) CNT/CdS NPs, and (c) CNT/silica NPs. Reprinted with permission from Ref [Li et al., 2006]. Copyright 2006 Wiley-VCH.

the photoinduced electron-transfer features, SWCNT/ZnPc-Py and SWCNT/H₂Pc-Py have been integrated into photoactive electrodes within the photoelectrochemical cells, revealing stable and reproducible photocurrents with monochromatic internal photoconversion efficiency values for SWCNT/ZnPc-Py as large as 15 and 23% without and with an applied bias of +0.1 V. In addition, Assali et al. [Assali et al., 2010] synthesized a new SWCNT-surface-modifier amphiphilile consists of a polyaromatic component resembling a butterfly topology with open wings, and a carbohydrate-tethered tetrabenzo(*a,c,g,i*)fluorene (Tbf) segment (compound 11 in Scheme 1). The resulting compounds exhibited more effective capacity to exfoliate MWCNTs in water than the pyrene-based amphiphilic carbohydrates, since the much stronger π - π interactions between the SWCNTs and Tbf groups. This enhanced interaction can be most likely ascribed to the ability of butterfly-like polyaromatic structure of Tbf to fit more effectively on the CNT surfaces. It is also found that the resulting surface-modified SWCNTs with a multivalent sugar exposition on their surface display selective binding with appropriate biological receptors.

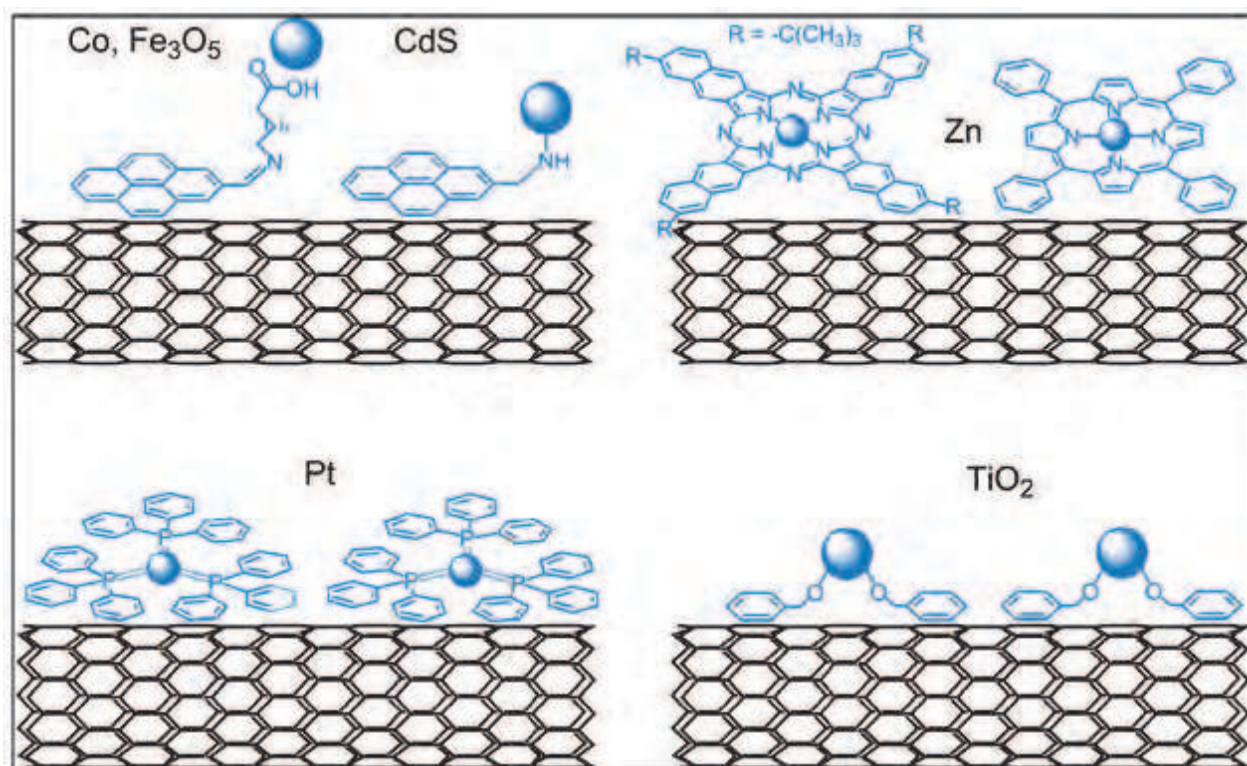


Fig. 2. Examples of linking agents and ligands used to attach inorganic NPs to pristine CNTs via π - π stacking interactions. Reprinted with permission from Ref. [Eder, 2010]. Copyright 2010 American Chemical Society.

In addition, direct assemblies of aromatic-compound-stabilized-NPs onto CNT surfaces through π - π stacking interactions provides a more facile route to fabricate CNT-based nanohybrids (Fig. 2) [Eder, 2010]. Such employed aromatic compounds tend to be terminated with functional moieties such as amine, thiol and carboxylic acid groups, which can interact with surfaces of specific NPs and thus stabilize them. Simultaneously, the remained aromatic ends enable those NPs to be anchored onto the CNT sidewalls by π - π stacking interactions, resulting in the formation of a variety of hybrid nanostructures. Following this strategy, Ou et al. [Ou & Huang, 2006] described the fabrication of CNT/Au NPs composites in aqueous solution using 1-pyrenemethylamine as the interlinker. The alkylamine substituent of 1-pyrenemethylamine binds to a Au NP, while the pyrene chromophore is noncovalently attached to the sidewall of a CNT via π - π stacking interaction. Such Au NPs with diameters of 2-4 nm can be successfully assembled on the MWCNT surfaces in a quite high density. It was also found that the attachment of Au NPs onto the CNT surfaces can largely quench the photoluminescence of 1-pyrenemethylamine and lower its emission intensity. Similarly, CdS, Co, Fe_3O_4 , Pt and TiO_2 NPs have also been directly assembled onto the CNT surfaces, yielding versatile hybrid nanostructures [Eder, 2010].

2.3 Other small molecular non-covalent CNT-surface-modifiers

Besides the ionic and aromatic-groups contained molecules, some other small molecular surfactants also have been utilized to non-covalently functionalize CNTs aimed to create varied CNT-based nanohybrids. For instance, Bourlinos et al. [Bourlinos et al., 2007] wetted

pristine CNTs with vinyl silane molecules via non-covalent interactions between the vinyl groups and CNT surface. After condensation to an oligomeric siloxane network and subsequent calcinations, silica nanoparticles with diameter ranging from 5 to 12 nm were generated and well-dispersed onto the CNT surfaces. Another approach to noncovalently modify MWCNTs was performed by embedding the CNTs within the polysiloxane micelles [Wang et al., 2006]. After a condensation process, a uniform polysiloxane shell formed around the CNT sidewalls. It was also found that the Au NPs can be in-situ generated and attached on the polysiloxane shells upon heating HAuCl₄ aqueous solution at 100 °C. Prolonging the heating process, the growing Au NPs can be further jointed and form continuous Au nanowires along the CNTs.

3. Polymeric CNT-surface-modifiers

Although a large number of hybrid nanostructures have been built on the basis of non-covalently surface-modify CNTs with small molecules, such resultant nanohybrids tend to lack of stability owing to the limit interaction sites between the small molecules and CNT sidewalls. As a promising alternative choice, amphiphilic linear polymers are often used to non-covalently functionalize CNT sidewalls, since they not only reduce the entropic penalty of micelle formation, but also have a significantly higher energy of interaction than small molecules with CNTs. So far, several types of such polymeric CNT-surface-modifiers have been developed. They can be categorized into polyelectrolytes and non-ionic polymers.

3.1 Polyelectrolytes

The choice of polyelectrolytes for non-covalent functionalization of CNTs endows CNT surfaces with positively or negatively charged properties, which provide a variety of opportunities to generate varied CNT-based hybrid nanostructures. This type of polymer generally contains multiple aromatic motifs which allow them to be directly attached onto CNT sidewalls via π - π stacking interactions and polymer-wrapping techniques. For example, the hydrolyzed poly(styrene-*alt*-maleic anhydride) (hPSMA) can be non-covalently adsorbed onto CNT surfaces from aqueous solutions via hydrophobic interactions [Carrillo et al., 2003]. Such attached hPSMA layer contained carboxylic groups, which were used as handles to further covalently attach poly(ethyleneimine) (PEI) and a cross-linked polymer bilayer was formed. These cross-linked polymer layers greatly enhanced the stability of the resultant CNT/polymer hybrids. By simply repeating these steps, a multilayered polymeric film consisting of alternate polyanionic and polycationic layers can be built up. On the basis of the terminated PEI layers, negatively charged Au NPs can be immobilized on the surfaces of CNT/polymer hybrids by means of electrostatic interactions. Another typical polyelectrolyte for CNT-surface-modification has been explored by Mountrichas et al. [Correa-Duarte et al., 2004]. They have synthesized an amphiphilic polystyrene-*b*-poly(sodium (2-sulfamate-3-carboxylate)isoprene) (PSHI) copolymer and utilized them to non-covalently functionalize MWCNTs. The hydrophobic polystyrene block of the polymer can interact with CNT sidewalls via π - π stacking and wrapping. While the hydrophilic polyelectrolyte block stands on the CNT surface towards the surrounding media, which not only enables the PSHI-modified CNTs to be well dispersed in water, but also provides anionic environment to cap cationic ions such as Cd²⁺. Followed by the addition of thioacetamide, CdS NPs were in-situ generated and attached onto the CNTs surfaces, leading to the formation of a CNTs/PSHI-CdS ensemble as a stable aqueous solution.

LBL techniques provide effective routes to assemble varied polyelectrolytes and charged functional components onto the CNT sidewalls to create versatile hybrid nanostructures. For instance, poly(styrene sulfonate) (PSS) containing both benzene groups and negatively charged sulfonate groups enable them to effectively functionalize CNTs surfaces, yielding a stable dispersion of individual CNT in water. By means of negatively charged sulfonate groups, the cationic poly(diallyldimethylammonium chloride) (PDDA) can be homogeneously adsorbed onto the surfaces of PSS-modified CNTs through the electrostatic interactions [Mountrichas et al., 2007]. Followed by LBL processes, negatively charged NPs such as Au@silica can be closely packed onto such surface-modified CNT sidewalls in a controllable manner depending on the number of layers deposited.

3.2 Non-ionic polymers

Although polyelectrolyte-modified CNTs provide versatile approaches to fabricate CNT-based hybrid nanostructures, they tend to be sensitive to the surrounding conditions such as pH value and ionic strength. These greatly limit the fabrication of CNT-based hybrids in varied reaction conditions. To avoid these intrinsic limitations, non-ionic linear and dendritic polymers have also been explored to non-covalently functionalize CNTs.

3.2.1 Linear polymers

An important type of non-ionic linear polymers for non-covalently functionalization of CNTs is block copolymer. Selective adsorption of block copolymer triggers a repulsion among the polymer-decorated CNTs and stabilizes the exfoliated CNTs in the dispersion. It has been found that the solubility of CNTs can be effectively manipulated the composition of the utilized copolymer. For example, Smalley group used polyethylene oxide-polypropylene oxide-polyethylene oxide (Pluronic PEO-PPO-PEO) triblock copolymers, selecting molecules with large PEO molecular weight to provide steric stabilization [Moore et al., 2003]. Similarly, Shvartzman-Cohen demonstrated that a large variety of di- and triblock copolymers in selective solvent (aqueous and organic) conditions also excellent stabilizing ability to SWCNTs [Shvartzman-Cohen et al., 2004a]. They also suggested that a proper choice of the polymer molecular weight may result in dimensional selectivity enabling purification of SWCNTs from mixtures of non-nanometric objects [Shvartzman-Cohen et al., 2004b].

More recently, Zou et al. [Zou et al., 2008a, 2008b] have explored to disperse CNTs in varied solvents and PS matrix using conjugated block copolymer of poly(3-hexylthiophene)-*b*-polystyrene (P3HT-*b*-PS). In such dispersion processes, P3HT blocks attached to CNT surfaces through π - π stacking interactions, while PS blocks located at the outermost surface of CNTs. The good solubility of PS blocks in various organic solvents (chloroform, tetrahydrofuran and toluene) and the compatibility with the PS matrix enhanced the solubility of CNTs in organic solvents and the dispersibility in PS matrix. Similarly, they also utilized a series of block copolymers such as P3HT-*b*-poly(methyl methacrylate), P3HT-*b*-poly(acrylic acid) and P3HT-*b*-poly(poly(ethylene glycol) methyl ether acrylate) (P3HT-*b*-PPEGA, Fig. 3) to non-covalently modified CNTs, and dispersed such surface-modified CNTs into various solvents and polymer matrices [Zou et al., 2009]. In addition, oligothiophene terminated poly(ethylene glycol) was also demonstrated to enable non-covalently functionalized CNTs and well disperse them in aqueous media [Lee et al., 2007]. As a more complexed system, Kim et al. [Kim & Jo, 2010] applied poly(vinyl benzyloxy

ethyl naphthalene)-*graft*-poly(methyl methacrylate) as compatibilizer, in which naphthalene units interact with MWCNTs via π - π interactions. While the poly(methyl methacrylate) units of the compatibilizer are miscible with poly(styrene-*co*-acrylonitrile) (SAN) matrix, which enable MWCNTs to be homogeneously dispersed in SAN matrix even in the presence of small amount of compatibilizer. Those resultant composites exhibited greatly improved mechanical properties and electrical conductivity as compared with those of composites without compatibilizer, since both the homogeneous dispersion of CNTs in SAN matrix and good interfacial adhesion between SAN and non-covalently compatibilizer-modified CNTs.

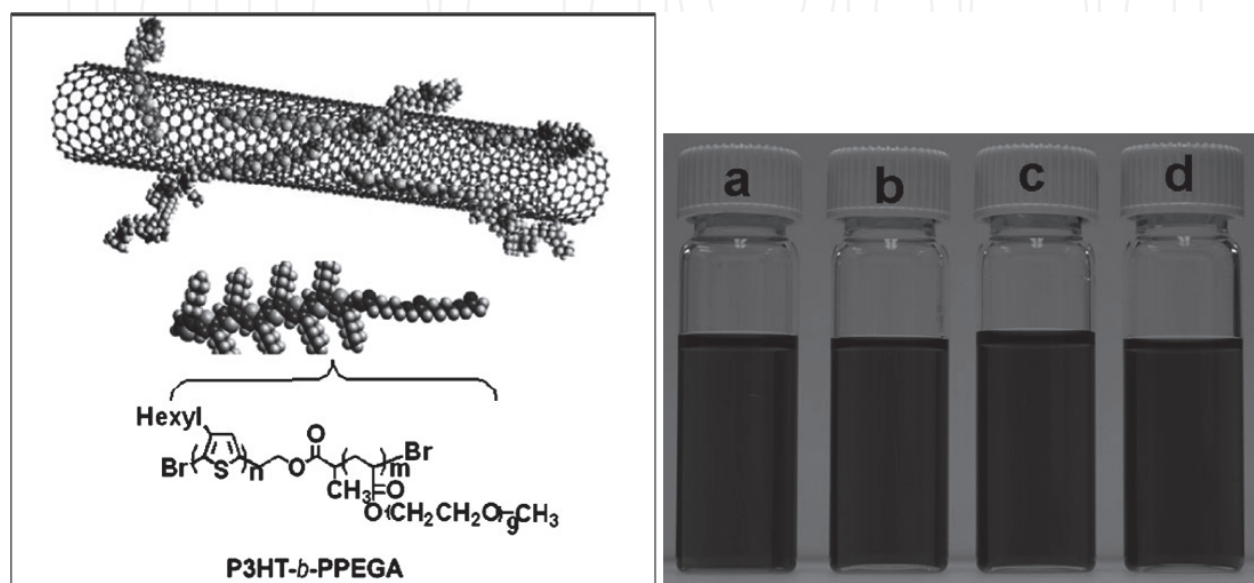


Fig. 3. (Left) Schematic illustration of dispersing and functionalizing CNTs by conjugated P3HT-b-PPEGA block copolymer; (Right) photographs of P3HT-b-PPEGA dispersed MWCNTs in a) chloroform, b) toluene, c) methanol, d) DMF. Reprinted with permission from Ref [Zou et al., 2009]. Copyright 2009 Wiley-VCH.

Besides the amphiphilic block copolymers, linear homopolymers with or without functional moieties, such as poly(vinyl pyrrolidone) and phospholipid-polyethylene glycol (PL-PEG) also can be used to non-covalently functionalize CNTs via relatively weak wrapping interactions [O'Connell et al., 2001; Welsher et al., 2009]. Using PL-PEG, Welsher et al. [Welsher et al., 2009] successfully debundled SWCNTs in aqueous media by means of a stabilizer-exchange process. The resulting SWCNTs suspension demonstrated an increase in quantum yield of more than one order of magnitude, while still maintaining the high biocompatibility. More importantly, the near-infrared photoluminescence emission of such modified-SWCNTs allow them to be used to perform cell imaging at a quite low dose.

Beyond the conventional synthetic linear polymers, biomacromolecules such as DNA can non-covalently modify CNTs sidewalls as well. So far, several groups have reported that DNA strands strongly interact with CNTs to form stable hybrids that can be effectively dispersed in aqueous solutions. In the case of wrapping CNTs with single-stranded DNA, DNA tends to self-assemble into a helical structure around individual nanotubes in such a way that the electrostatics of DNA-CNT hybrid depends on tube diameter, electronic properties, particular DNA sequence and length of sequence, enabling not only to separate

metallic fractions from semiconducting tubes but also to perform a diameter-dependent separation via ion exchange chromatography [Zheng et al., 2003; Tu et al., 2009]. Mediated by chemical linkers, DNA can be physically attached onto CNT surfaces, which provides an indirect alternative to fabricate CNT/DNA hybrids. For example, using pyrene methylammonium compound as a chemical linker, 2/3 of CNTs were anchored with DNA strands by means of electrostatic interactions between the ammonium moieties of linkers and the phosphate groups of DNA backbones [Xin et al., 2003]. Similarly, Taft et al. [Taft et al., 2004] attached pyrene-modified oligonucleotides onto the CNT sidewalls through hydrophobic interactions. To visualize the immobilized DNA strands, complementary sequences were thiolated and attached to Au NPs, which offers a direct visualization strategy to analyze CNT/DNA conjugates by scanning electron microscopy.

For CNT/DNA hybrid nanostructures, the combination of DNA-based biomolecular recognition principles and outstanding electronic properties of CNTs make them very ideal for the construction of electrochemical sensors, biosensors and electronic devices. Also, the 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. The advances in the relevant field have been well reviewed in the recent publications [Daniel et al., 2007; Jacobs et al., 2010; Zhang et al., 2010].

3.2.3 Dendritic polymers

Although the conventional linear polymers including polyelectrolytes and block copolymers have been extensively used to non-covalently functionalize CNTs, there exist two main shortcomings derived from the intrinsic properties of such employed polymers: 1) the amphiphilic block copolymers tend to form free micelles which are hardly removed from the CNT/polymer suspensions; 2) the polyelectrolytes are very sensitive to the surrounding media, which hinders the extensive manipulation of CNT/polymer hybrids in varied conditions. Moreover, targeted to assembly of varied functional components onto CNT surfaces, most of the reported CNT-surface-modifiers generally lack of multifunctionalities and thus those non-covalently modified CNTs were only efficient to anchor either certain metal NPs or inorganic oxides. Therefore, more general type of CNT modifiers is highly desired to fabricate various types of stable and versatile CNT-based nanohybrids.

In our group, we recently synthesized pyrenyl moieties decorated hyperbranched polyglycidol (pHBP) and employed them as a novel CNT-surface-modifier *via* non-covalent processes [Li et al., 2010]. The pHBP macromolecule consists of dendritic units, linear polyether segments and numerous terminal hydroxyl and pyrene groups, which provides a three-dimensional dendritic globular architecture (Fig. 4). In comparison with the reported modifiers, the unique molecular structure of pHBP molecules makes them particularly suitable for fabricating versatile CNT-based nanohybrids by means of non-covalent techniques owing to the following reasons: 1) multiple pyrene moieties bearing on the periphery of pHBP can be tightly attached onto the CNT surfaces through π - π stacking interactions; 2) the uniform molecular composition of pHBP allows free pHBP to be easily removed from the CNT/pHBP sols using pure solvent; 3) the dendritic polyether structure of pHBP provides void-containing electron-negative environment, which is well-suitable to attract metal ions to be *in-situ* reduced to form and accommodate metal NPs; 4) the hydroxyl

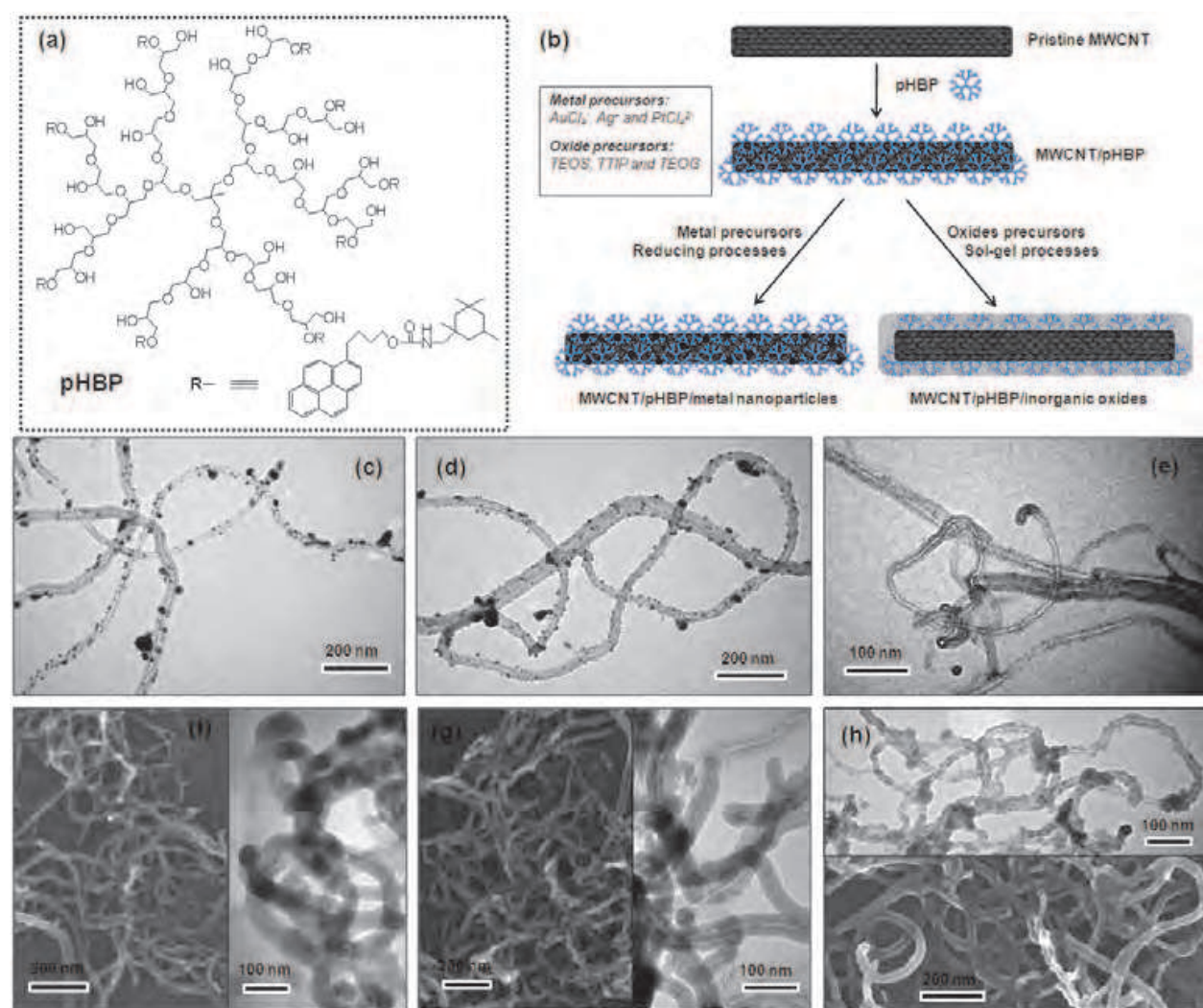


Fig. 4. Schematic illustration of molecular structure of pHBP (a) and the preparation of varied CNT/metal NPs and CNT/oxide hybrid nanostructures based on the non-covalently modified CNTs with pHBP (b); TEM images of CNT/pHBP/Au NPs (c), CNT/pHBP/Ag NPs (d), and CNT/pHBP/Pt NPs (e) hybrid nanostructures; SEM and TEM images of CNT/pHBP/SiO₂ (f), CNT/pHBP/GeO₂ (g), and CNT/pHBP/TiO₂ (h) nanofibers. Reprinted with permission from Ref [Li et al., 2010]. Copyright 2010 Wiley-VCH.

groups bearing on the periphery of pHBP facilitate the *in-situ* nucleation and growth of inorganic oxides via a sol-gel process, resulting in the formation of CNT/pHBP/inorganic oxides nanohybrids. This is the first report on the non-covalent functionalization of CNTs using three-dimensionally spherical macromolecules towards a general synthetic strategy for the efficient fabrication of CNT/pHBP/metal NPs and CNT/pHBP/inorganic oxide nanofibers. We also found that both the CNT/pHBP/Pt NPs and the CNT/pHBP/Au NPs hybrids showed excellent catalytic activity towards the reduction of 4-nitrophenol. In addition, rhodamine 6G was successfully incorporated into the CNT/pHBP/SiO₂ matrix, resulting in fluorescent nanohybrids. It is believed that these as-synthesized CNTs-based heterogeneous nanohybrids are promising for a wide range of applications in catalytic, energetic and bioengineering filed.

4. Conclusions

This chapter provides a comprehensive description for the fabrication of various CNT-based hybrid nanostructures mediated by a wide range of non-covalent CNT-surface-modifiers including small molecular surfactants, functional polymers and biomacromolecules. In such fabrication processes, the choices of non-covalent CNT-surface-modifiers not only enable the CNTs to be homogeneously suspended in various media, but also provide a wealth of opportunities to assembly additional functional components on CNT sidewalls to generate versatile hybrid nanostructures.

Although the great advances in the non-covalent assembly of functional components onto the CNT sidewalls have been achieved, several critical issues still remain to be suitably addressed. One of the most challenging topics is how to guarantee a mechanical stability of CNT-based hybrids obtained via non-covalent routes. In comparison with the covalent bonding, non-covalent attraction is less sufficient to tightly tether functional components onto CNT sidewalls. In this direction, it is a promising pathway to design novel CNT-surface-modifiers which either can interact with CNTs via relatively strong attractions and/or provide multiple interaction sites with CNT sidewalls. The second challenge involves the effectively non-covalent de-bundling and dispersion of SWCNTs in varied media. Although SWCNTs possess more excellent properties compared with MWCNTs, they tend to aggregate into bundles and ropes due to the strong van der Waals interactions between each other derived from their high polarizability and smooth surface. So far, substantial efforts have been done to overcome that shortcoming. Unfortunately, relatively less satisfied outcomes involving the obtainment of individual SWCNTs have been achieved, which sets a main barrier to produce more SWCNT-based hybrids targeted extensive applications. In this case, the design and synthesis of new type of CNT-surface-modifiers are highly desired.

In addition, a successful application of CNT-based hybrid nanomaterials and their implementation into the market requires a strong improvement in methodology to ensure reproducibility and better understanding the structure-property relationship. Considering the possible health and safety issues aroused by the use of nanomaterials in biological and medical field, it offers a promising resolution to develop complete green protocols to fabricate such hybrid nanomaterials. In the meantime, it is equally important to address the biocompatibility of the hybrid materials by the further detailed studies on their toxicology and exposure.

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Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

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