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Carbon Nanotubes Engineering Assisted by Natural Biopolymers

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1. Introduction

For the application of carbon nanotubes (CNTs), there are many practical problems to be solved. Large scale as-produced CNT especially single-walled CNTs (SWCNTs) inevitably contain impurities that produced in their growth process（Huo, et al. 2008) As-produced SWCNTs normally are of different chirality (Kataura, et al. 1999) Untreated CNTs are of high surface area and align into big bundles for their strong Van Der Waals attraction. The high aspect ratio and strong attraction between CNTs further leads to the physically entanglement of CNT ropes. The strong aggregation of CNTs gives rise to a highly complex network makes their uniformly dispersion into other substances hard to be achieved (Mitchell, et al. 2002). Engineering CNTs thus need variety of technologies to achieve CNT purification, separation, dispersion, stabilization, alignment, functionalization and organization (Baughman, et al. 2002). Many physical and chemical approaches have been developed to achieve these goals since the discovery of CNTs (Tasis, et al. 2006). On the route to the engineering of CNTs, biopolymer covalently and noncovalently functionalization of CNTs has been found to be promising way in highly effective realization these technologies. Initial great progress on dispersion of CNTs (Barisci, et al. 2004), CNT liquid crystal phase formation (Badaire, et al. 2005) and selective chiral SWCNTs enrichment (Zheng, et al. 2003) assisted by biopolymer DNA reveal that biopolymers are promising agents for high quality CNT materials preparation, which has soon attracted wide attentions on biopolymers assisted CNT engineering. Now widely obtainable, large scale production and low price agent polysaccharides have been found to be easier and commercially acceptable for achieving such goals. High concentration CNTs single dispersion and stabilization could be simply achieved by varieties of polysaccharides such as chitosan (Zhang, et al. 2007), gellan gum (Panhuis, et al. 2007), hydraulic acid (Moulton,et al. 2007) and etc. Physical purification of CNTs by chitosan funcitonalization has been approved to be easy processing and effective (Yang, et al. 2006). Aligning CNTs through liquid crystal phase of CNTs dispersed by polysaccharides has also been developed. The stable dispersed CNTs by biopolymers were further introduced into biomedical applications such as tissue engineering and drug delivery system, which broaden the application range of CNTs. For the bioactivity of biopolymers, their composites with CNTs provide excellent sensing performance. The biomimetic actuation based on CNT/biopolymer devices have also initially been shown to be of large and fast actuation displacement under low voltage electrical stimulation.

2. Supramolecular self-assembly of biopolymers onto CNT surface

To engineering CNTs, such as dispersion CNTs into solution for further manipulation or preparing CNT composite materials, functionalization of CNTs is usually adopted. There are two approaches for CNT functionalization, covalent and noncovalent as illustrated in figure 1 (Hirsch, 2002). Prestine CNT surface could be chemically modified through oxidation and grafting processing or reversibly absorbing amphiphilic molecules.

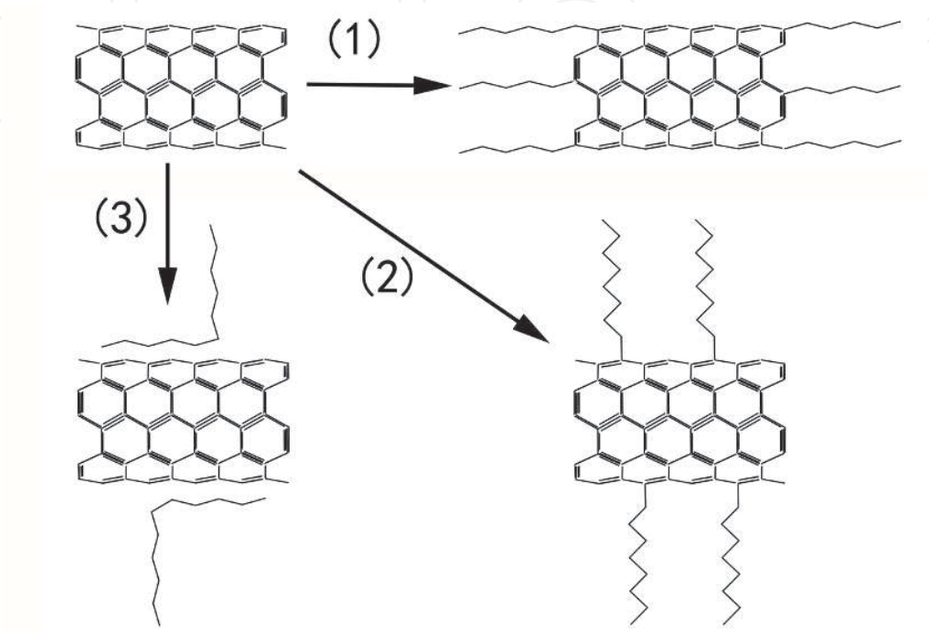


Fig. 1. Schematic illustration for the covalent end (1) and side wall (2) functionalization of CNTs by oxidation and grafting reaction and noncovalent (3) functionalization of CNTs by surface absorbing amphiphilic molecules.

The covalent bond attaches functional groups on the side wall or end of CNTs to obtain desired functions. Covalent approach inevitably changes the intrinsic electrical, mechanical and thermal properties of CNTs, which are important for their variety of applications. However, the strong covalent bond between molecules and CNTs also has advantages in many aspects (Balasubramanian, et al. 2005; Dyke, et al. 2004; Banerjee, et al. 2005). For example, it could reinforce interfacial adhension between CNTs and composite matrix. Covalently functionalized CNTs could be used as stable nano-template for further supramolecular assemble of target molecules. Covalently functionalization of CNT could be controlled to adjust electrical performance of functionalized CNTs that may have higher sensitivity of target molecules.

The noncovalent functionalization of CNTs based on the supramolecular chemistry theory (Lehn, 1985) studies the organization of molecules with CNTs through weak interactions that provide variety of functions without changing CNT properties. The weakly absorbed biopolymers could be removed by varying the solution environment, which favours the realization of CNT excellent electrical, mechanical, thermal and interfacial performances. The surpramolecular chemistry of CNTs for the noncovalent functionalization of CNT (Zhao, & Stoddart 2009) has thus been intensively studied for the CNT engineering. In this

field, of biopolymer noncovalent functionalization of CNT has attracted great attentions for their important roles in variety of CNT applications.

Earlier than theoretical understanding the interaction mechanism between biopolymers and CNTs, helical crystallization of proteins on CNTs has been experimentally observed earlier in 1999 and attributed to order structure of hydrophobic CNT surface (Balavoine, et al. 1999). Later researches have shown that CNTs are effective on reinforcing the crystallization of biopolymers such as bombyx mori silk, poly(L-lactide), poly(ε-caprolactone), polyhydroxyalkanoates and streptavidin. (Levi, et al. 2004; Ayutsede, et al. 2006; Yun, et al. 2008; Wu, et al. 2006). To understand the mechanism of CNT induced biopolymer crystallization, FTIR online test method was adopted to analyze the influence of CNTs on the crystallization of biopolymer poly(L-Lactide) and reveal that CNT reinforced biopolymer crystallization is originated from surface induced biopolymer conformational order. (Hu, et al. 2009) A recent study also show that CNT could reinforce the piezoelectric actuation performance of regenerated cellulose while the reinforced crystalline is in agreement with it. (Yun, et al. 2007).

The widely used polysaccharides amylose (Kim, et al. 2003), chitosan (Zhang, et al. 2007), hydraulic acid (Moulton, et al. 2007), gellan gum [Panhuis, et al. 2007] and cytlodextrin (Komatsu, et al. 2008) have been found to be helically wrapped on CNT surface. As has been shown in figure 2, the biopolymer chitosan helically wrapped on CNT surface, which favour CNT solubilisation in water. Some theoretical calculations prove the helical wrapping on CNTs is the optimal configuration for polymers of rigid molecular chains (Xie, et al. 2005; Gurevitch, et al. 2007). Recent experiment revealed that the absorption of biopolymer chitosan on CNT surface influence by the deacetylation degree of chitosan molecular chain (Iamsamai, et al. 2010). Low deacetylation degree provide more hydrophobic sections that favour the absorption of chitosan on CNT surface and results in better stability of CNT suspension in the experiment though high deacetylation degree provide higher electrostatic repulsive force that should favour the stabilization of CNTs as colloidal. This interesting solution behaviour of chitosan wrapped CNTs reveals that the interaction between biopolymer and CNT surface is more important for their stabilization than the traditional key issues that determine colloidal behaviours.

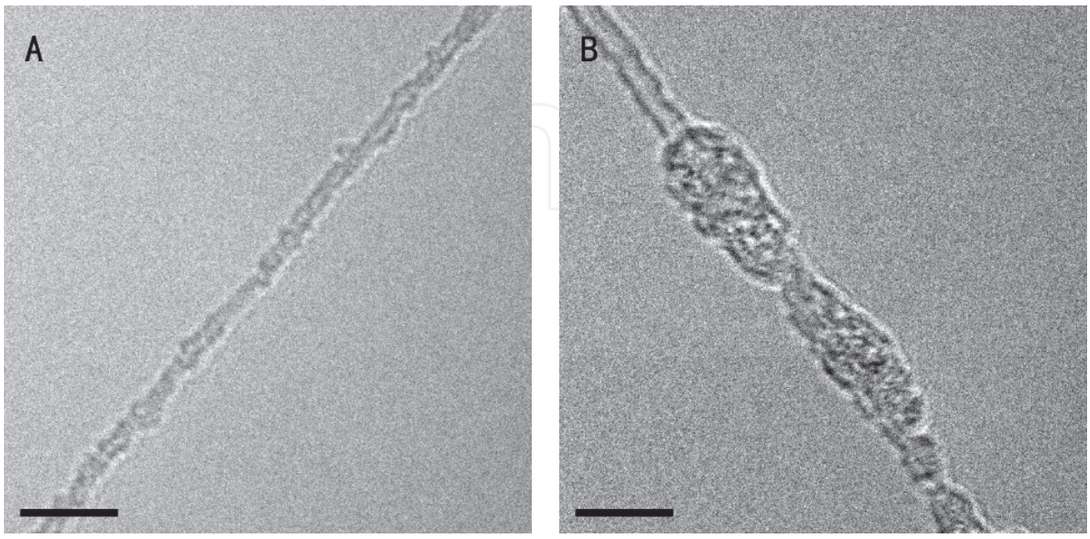


Fig. 2. (A) Single helical and (B) double helical wrapped CNTs, scale bar 5 nm.

The interaction between DNA and CNT surface has been intensively studied (Johnson, et al. 2010; Gao, et al. 2008; Shtogun, et al. 2007). DNA molecular chain composes of four bases adenine (A), cytosine (C), guanine (G), and thymine (T). They have been experimentally and theoretically approved to be of high affinity contact with CNT sidewalls. Very recent research compared the energy variation for the binding of four bases with CNT in water. The interactions of water-CNT, water-bases and base-CNT have been found to important for the binding free energy of the four bases with CNT in water separately. As a result the base's affinity for CNT binding follows the trend G>A>T>C. Base–CNT interactions are dominated by π–π stacking interactions with solvent and entropic effects playing a minor. The sequence of DNA motifs further influences their absorption on CNT surface and their stability in water.

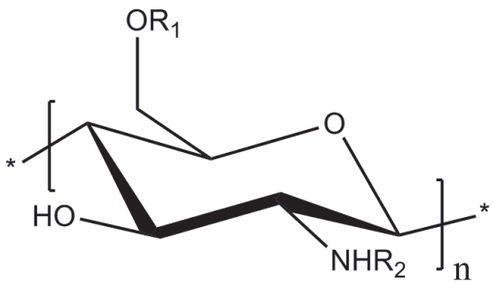
3. Dispersion and stabilization of CNTs assisted by biopolymers

The initially works on studying the cooperation of biopolymers with CNTs were to assist CNT dispersion (Kim, et al. 2003). To understand the dispersion and stabilization of CNTs in water by biopolymers, we should first study the interaction between CNTs and water for the assembly of biopolymer onto CNT surface is mostly achieved in water environment and the assembly indeed forms on the CNT-water interface of unpolar-polar interfacial inducement force. As we have mentioned above, pristine CNTs have the strong attendance to aggregate in water making their dispersion in water without surface treatment hard. In recent years there have been a lot of researches on understanding the mechanism of CNT aggregation in water. A typical molecular dynamic stimulation has theoretically attributed the aggregation of CNTs to the solvation interaction of polar water molecules around unpolar CNTs surface (Walther, et al. 2001). This solvation interaction causes the hydrogen atoms of water molecules point to the surface of CNTs, leading to higher orientation of water molecules around CNT surface than that in the bulk water. The orientated water molecules give a rise in the energy of those molecules around CNTs and force CNT aggregate into bundles to minimize the system energy rise.

Some very initially works has been done to solve this problem by the chemical modification of CNT surface, transferring hydrophobic unpolar CNT surface into hydrophilic polar one. However, the chemical modification of CNT create large amount of defects on CNT surface, leading to the variation of intrinsic CNT electronic structure, which changes the electric performance of CNTs and limits the application of CNTs in variety of fields (Robinson, et al. 2006).

For comparison, physical approach that is called noncovalent functionalization has been found to be a promising method for the preservation of intrinsic CNT surface structure and their variety of properties. This approach was initially proposed in 2001 for the PVP assisted dispersion of CNT in water (O'Connell, et al. 2001). The supramolecular self assembly of small molecules such as lipid derivatives on CNT surface has been detailed studied in 2003 (Richard, et al. 2003). The CNT-water interface direction the ordered structure of lipid derivatives onto CNT surface could lower the system energy. After that, non-covalent functionalization of CNTs by supramolecular self-assembly of biopolymers on CNT surface has been found to be of excellent effect for CNT dispersion. Gum Arabia, the ancient biopolymer dispersant was introduced to stabilize SWCNTs. The dispersion could be

concentrated into suspension of SWCNT concentration as high as 150 mg/mL, the highest concentration for SWCNTs (Bandyopadhyaya,et al. 2002). The Hyaluronic acid functionalized CNTs at high concentration of 10mg/mL shows anisotropic birefringence phenomenon, indicating the liquid crystal phase of biopolymer functionalized CNTs.
Within all those biopolymers functionalized CNTs, Chitosan wrapped CNT is one of most important one for their potential application in variety of fields, such as drug delivery, tissue engineering, electrochemical sensing and actuation. Chitosan wrapped CNTs could be directly dispersed at concentration of 3mg/mL (Lynam, et al. 2007). However, chitosan wrapped CNT could only stabilized in acidic solution. In year 2007 Zhang et al. investigate solution behaviours of chitosan wrapped CNTs (Zhang, et al. 2007). To reveal the influence of electrostatic interaction on the stabilization of chitosan wrapped CNT, derivates of chitosan has been used as shown in figure 3. The groups that containing $-NH_2$ and –COOH would only be charged in acidic and basic environment separately while the group $CH_2CHOHCH_2CN(CH_3)_3^+Cl^-$ charges in the whole pH range.



R_1=H or CH_2COOH

R_2=H
or CH_2COOH
or $C{=}OCH_2CH_2COOH$
or $CH_2CHOHCH_2CN(CH_3)_3^+Cl^-$

Fig. 3. Molecular structure of chitosan and its derivates

The comparative characterization indicates that electrostatic repulsive force of the charged chitosan and its derivate molecular chains could stabilize their wrapped CNTs. The aggregation of chitosan and its derivate wrapped CNTs happens when they were discharged by changing the pH value of their suspension. When the pH value of suspension for chitosan wrapped CNTs is higher than 6.59, the $-NH_3^+$ group deprotonated into $-NH_2$ and precipitate could be observed. The CNTs functionalized by chitosan derivates that contains COOH group deprotonate in acidic environment of pH lower than 4.66 aggregate. The chitosan derivate containing group $CH_2CHOHCH_2CN(CH_3)_3^+Cl^-$ show no aggregation in whole pH range. But the aggregation mechanism has not been fully understood. Amylase, which has very similar structure of chitosan and no charge group on its molecular chain, can also stabilize CNT in water. As has been mentioned above, the impact of deacelytation degree on CNT stabilization reveals the electrostatic force is not the dominant fact for chitosan wrapped CNT stabilization. Some research found that the ammonia group in chitosan molecular chain has strong affinity to CNT surface (Long, et al. 2008). Previous research has also shown that the interaction between chitosan and CNT are chiral dependant. Considering chitosan itself aggregates in water in the neutral and basic pH range while chitosan oligosaccharide, which has the same molecular structure of chitosan but shorter chain length, could be solubilized in neutral and basic solution, the molecular chain length should also has impact on chitosan wrapped CNT stabilization. Thus the full image of chitosan wrapped CNTs stabilization mechanism is still complicated and unclear. Further investigation is needed.

4. Purification and selective enrichment SWCNTs by biopolymers

Commercially available CNTs large scale produced by either arc discharge or chemical vapor deposition methods inevitably contain carbonaceous impurities as shown in figure 4. Those impurities not only largely lower the performance of CNTs and their composite materials but also invalid the manipulation of CNTs as micro system devices. To remove those impurities, purification of CNTs has been studied for more than ten years. Though lots of chemical approach has been widely studied for multi-walled CNTs and few-walled CNTs, purification of SWCNTs is still a problem for the chemical durability of SWCNT is too weak to be remained when the carbonaceous impurity removed.

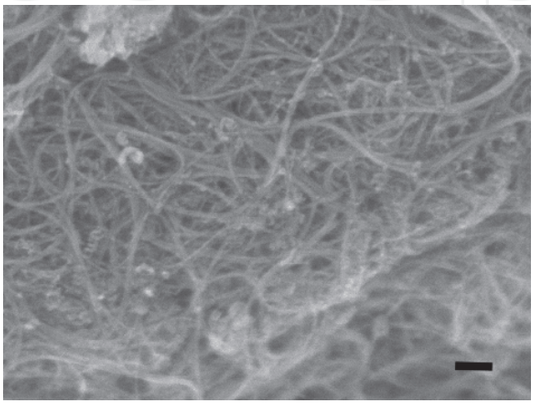


Fig. 4. Scanning electron microscopic image for raw SWCNTs, scale bar 100 nm.

Impurities and CNTs are of different elements, structure, size, density, which lead to their different chemical and colloidal behaviours. The surface properties of impurities should also be different from that of CNTs especially the interaction with biopolymers. In this aspect, biopolymers show incomparable efficiency. In year 2002, amylose functionalized SWCNTs could be purified for the better affinity of amylose to SWCNTs than carbonaceous impurities. (Star, et al. 2002). In our experiment, as shown in figure 5, we also found that gellan gum functionalized SWCNTs could also be separated from carbonaceous impurities by centrifuging their co-suspension (Lu, & Chen, 2010).

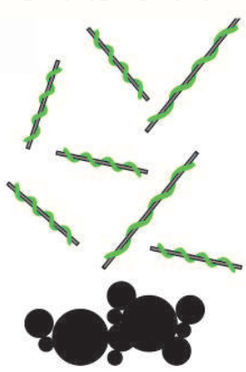


Fig. 5. Purification of CNTs by the stonger affinity of biopolymer onto CNTs (the upper suspended units) than that of impurities (the bottom aggregated units)

Beside the removal of carbonaceous impurity, further purification of SWCNTs requires sorting SWCNTs of different chiralities. Biopolymers are not only capable of separating SWCNT from carbonaceous impurities but also show high efficiency on selective enriching specific chiral SWCNTs. As we know that metallic and semiconducting SWNTs are different in several aspects, in addition to their obvious differences in electrical conductivity, including static polarizability and surface characteristics, chemical reactivity, and so forth. They are also associated with SWNTs of different diameters.

In year 2003 Zheng et al found that anionic exchange column could separate ssDNA wrapped metallic SWCNTs from that of semiconductive ones (Zheng, et al. 2003). It was attributed to the different polarizability of metallic and semiconductor SWCNTs, which results in their different interaction of negative charged ssDNA that wrapped on them. Further detailed design of ssDNA sequence, selective harvesting of 12 major single-chirality SWCNT could be achieved through ion-exchange chromatography (Tu, et al. 2009). Separation of chiral SWCNTs could also be achieved by polysaccharides. Chitosan was found to have ability for the enrichment of small-diameter semiconducting SWNTs by preserve the as-dispersed suspension overnight without centrifugation or any other physical treatment (Yang, 2006). After that, another polysaccharide agarose were introduced to separate metallic and semiconducting SWCNTs (Tanaka, et al. 2009; Tanaka, December 2009; Tanaka, et al. 2010; Liu, et al. 2010). The suspension of single dispersed SWCNTs by surfactant SDS was mixed with agarose gel for gelation. The gel containing SDS-dispersed SWCNTs was frozen, thawed, and squeezed to yield a solution of enriched (70%) metallic SWCNTs. The semiconducting SWCNTs (95%) were left in the gel (Tanaka, & Suga, 2009). The same separation was later demonstrated on column based gel chromatography (Tanaka, & Nishide, 2009). The mechanism for agarose assisted separation of chiral SWCNTs is unclear. Some very recent involvement found that the separation effect originated from two main factors, the unique interaction of semiconductor SWCNTs with agarose gel and exfoliation of SDS molecules from SDS functionalized SWNT entities which may cause the precipitation of semiconductor SWCNTs in the gel (Li, et al. 2010). Thus understanding the role of SDS in the separation, it is possible to further optimize the purification of each fraction and develop a more effective and low-cost separation strategy. This method is more amenable to scaling up than the density gradient ultracentrifugation or ion-exchange chromatography.

5. Formation of CNT liquid crystal phase assisted by biopolymers

Single CNT is anisotropic unit for the high aspect ratio of cylindrical graphene nanostructure. The excellent performance such as electrical, mechanical and thermal performance of CNTs refers to the performance in axis direction. However, the bulk materials of CNTs show no anisotropic performance for their disordered structure. Thus the alignment of CNTs is of great value to obtain high performance CNT bulk materials. Though aligned CNT arrays could be obtained by CVD method, they are normally perpendicular to that of membrane surface. And a more important fact is that the large-scale macroscopic membrane is hard to obtain, which seriously limits the realization of their full potential. In recent years, aligning CNTs by processing disordered CNTs (Jin, et al. 1998; Safadi, et al. 2002; De Heer, et al. 1995, Casavant, 2003; Vigolo, et al. 2000) with external forces, such as electrical force, mechanical force, and liquid flow, has been widely studied. In this field, we have (Chen, et al. 2005) explored the method of aligning CNTs in polyurethane

by solvent-polymer interaction. Using this method, the Young's modulus of composite material has been obviously increased. But the weight fraction of CNTs in the polymer matrix is so low that the anisotropic performances of CNTs are still not well embodied.

Fig. 6. Schematic illustration of CNT phase transition from isotropic (left) to anisotropic (right) phase

Since the discovery of CNT alignment in liquid crystal phase in 2003 (Song, et al. 2003), the formation of CNTs liquid crystal phase has been extensively studied. CNT liquid crystal is lytropic, which caused by the volume effect of high aspect ratio CNTs as illustrated in figure 6 (Zhang, et al. 2006). To obtain CNT liquid crystal phase, high CNT concentration is needed and has been obtained by dispersion CNTs in super strong acid solution (Davis, et al. 2009; Davis, et al. 2004; Rai, et al. 2006). However, those solutions are not suitable for composite material preparation, which the mild solution processing is required.

For biopolymer could disperse CNT at high concentration, the anisotropic birefringence phenomenon of liquid crystal phase was earlier found in 2005 for DNA stablized CNTs (Badaire, et al. 2005). Later the spontaneous nematic phase separation of CNTs stabilized in aqueous biological hyaluronic acid solutions was also observed (Moulton, et al. 2007).The initially obtained SWNT dispersion is isotropic single-phase. Over time, the uniform isotropic phase separated into dispersions containing birefringent nematic domains in equilibrium with an isotropic phase. The time required for phase separation to occur depends on the concentration of SWNT and hyaluronic acid. The attractive interactions between the SWNT and HA shifts the onset of the phase separation toward lower concentration. This phase separation is accompanied by an increase in the dispersion viscosity with this increase qualitatively matching the degree of phase separation. The further development in 2008 has shown that mechanical shearing could uniformly align lyotropic nematic aqueous suspensions in thin cells (Zamora-Ledezma, et al. 2008) by drying the nematic CNT suspension, homogeneous anisotropic CNT thin films can be prepared. To quantitatively estimate the dichroic ratio of CNTs, optical transmission between parallel or crossed polarizers was characterized and analyzed. The order parameter for the anisotropic thin film was measured using polarized Raman spectroscopy and found to be quite weak. It was attributed to the possible entanglement of the CNTs and the intrinsic viscoelastic behavior of the CNT suspensions. In our very recent work, we found that the purity of CNTs is crucially important for CNT alignment (Lu, & Chen, 2010). Highly purified CNTs showed dominant nematic phase of domains as large as hundred micrometers as shown in figure 7a. The mechanical shearing treatment for the CNT liquid crystal phase could further obtain wavy aligned CNTs of typical band structure of polarizing microscope image as shown in figure 7b. The ordered parameter for this aligned was found to be as high as 0.88. The anisotropic electrical performance was characterized. The calculated resistivity in the parallel direction is as low as 1.477×10^{-4} Ωm, about one fourteenth of resistance in perpendicular direction.

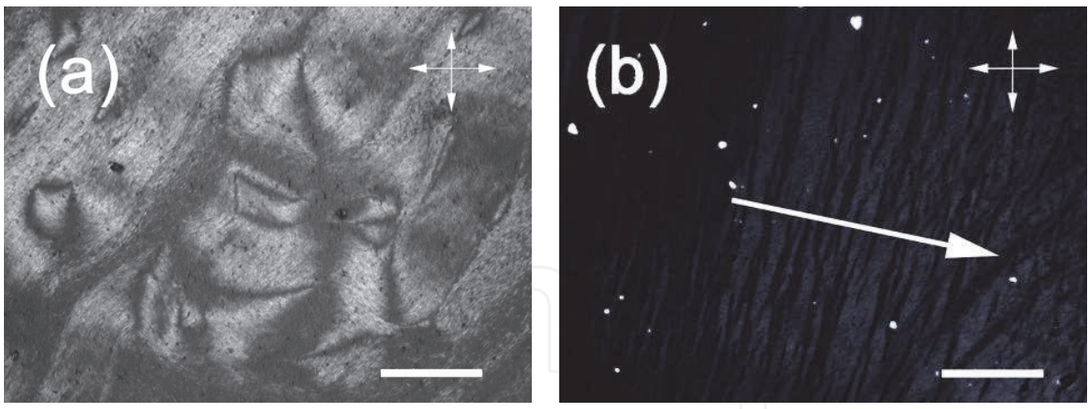


Fig. 7. Polarizing bireflection microscopic images for solid state composite membrane obtained from (a) unsheared and (b) sheared condensed gellan gum/CNT suspension between cross polarizers (scale bar 200 μm)

6. Biopolymer/CNT hybrids for drug delivery

CNTs especially SWCNTs are of surface area as high as 2600 m2/g, which is very suitable to be drug carrier for biomedical applications. Alberto Bianco initially introduced CNT as a template for presenting bioactive peptides to the immune system (Pantarotto, et al. 2003). B-cell epitope of the foot-and mouth disease virus (FMDV) was covalently attached to the amine groups functionalized CNTs. As a result, the peptides around the CNT adopt the appropriate secondary structure due to the recognition by specific monoclonal and polyclonal antibodies. The immunogenic features of peptide–CNT conjugates were subsequently assessed in vivo (Pantarotto, et al. 2003). Immunisation of mice with FMDV peptide–nanotube conjugates elicited high antibody responses as compared with the free peptide. These antibodies were peptide-specific since antibodies against CNT were not detected. In addition, the antibodies displayed virus-neutralising ability. The use of CNT as potential novel vaccine delivery tools was validated by interaction with the complement (Salvador-Morales, et al. 2006). The complement is that part of the human immune system composed of a series of proteins responsible for recognising, opsonising, clearing and killing pathogens, apoptotic or necrotic cells and foreign materials. Pristine CNT activate the complement following both the classical and the alternative way by selective adsorption of some of its proteins. Because complement activation is also involved in immune response to antigens, this might support the enhancement of antibody response following immunisation with peptide–CNT conjugates.

Kam et al. initially tried to deliver ssRNA into cells through functionalized CNTs in year 2005 (Kam, et al. 2005). Later, researchers have found that functionalized CNTs can cross the cell membrane (Martin, et al. 2003; Pantarotto, et al. 2004). Carbon nanotubes can be used to facilitate delivery of DNA or any bioactive agent to cells. While they can be functionalized to attach either electrostatically or covalently to DNA and RNA, the remaining unfunctionalized and hydrophobic portions of the nanotubes can be attracted to the hydrophobic regions of the cells. Biotin functionalized carbon nanotubes were bound to fluorescent dyes were capable of intercellular transport of fluorescent streptavidin (Kam, et al. 2004). Besides heterogeneous functionalization, carbon nanotubes could provide localized delivery of therapeutic agents triggered by external sources. Previously, it was

shown that carbon nanotubes absorb NIR light at wavelengths that are optically transparent to native tissue. For example, irradiation with a 880nm laser pulses can induce local heating of SWNTs in vitro thereby releasing its molecular cargo without harming cells or can be internalized within a cancer cell and with sufficient heating kill the cell (Kam, et al. 2005). This could allow selective delivery of drugs to certain cell types, helping to control the distribution of such cells throughout the engineered tissue. Modulated release of dexamethasone from chitosan/CNT composite has been show to be faster than traditional method (Naficy, et al. 2009).

7. Biopolymer/CNT composite as tissue scaffolds

CNTs are famous filler for reinforcing the mechanical performance of polymer matrix. Thus the very important aspect in biomedical application of CNTs is for structural support. By dispersing a small fraction of CNTs into a polymer, significant improvements in the mechanical strength of the composite have been observed. For example, MWCNTs blended with chitosan showed significant improvement in mechanical properties compared with those of chitosan (Wang, et al. 2005). The composite composed of 2wt% MWNT shown more than doubled Young's modulus and tensile strength compared to neat chitosan. Tuning of the mechanical properties of the polymer can be adjusted depending on CNT loading and with the need of very small amounts may counterbalance their high structure stability. In vitro work has shown that several different cells types have been successfully grown on CNT/biopolymer composites. MacDonald found that blends of SWNT with collagen support smooth muscle cell growth (MacDonald, et al. 2005). L929 mouse fibroblasts have been successfully grown on CNT scaffolds (Correa-Duarte, et al. 2004) Abarrategi et al. demonstrates the use of scaffolds composed of a major fraction of MWCNT (up to 89wt%) and a minor one of chitosan, and with a well-defined microchannel porous structure as biocompatible and biodegradable supports for culture growth. Cell adhesion, viability and proliferation onto the external surface of MWCNT/CHI scaffolds with C2C12 cell line (myoblastic mouse cell), which is a multipotent cell line able to differentiate towards different phenotypes under the action of some chemical or biological factors, has been evaluated in vitro and quantified by MTT assays. The evolution of the C2C12 cell line towards an osteoblastic lineage in presence of the recombinant human bone morphogenetic protein-2 (rhBMP-2) has also been studied both in vitro (e.g., following the appearance of alkaline phosphatase activity) and in vivo (e.g., by implantation of MWCNT/chitosan scaffolds adsorbed with rhBMP-2 in muscle tissue and evaluation of the ectopic formation of bone tissue) (Abarrategi, et al. 2008).

8. Biopolymer/CNT composite sensor

Tracking biological behaviours of cells, organs, blood and etc are of great value for the development of biomedical engineering. CNTs are of high. To monitor engineered tissues, we could use implantable sensors capable of relaying information extracorporeally. Such a sensor would provide real time data related to the physiological relevant parameters such as pH, pO2, and glucose levels. CNT/biopolymer composites are of excellent mechanical performance as has been mentioned above. The good biocompatibility with high electrical and electrochemical sensitivity is advantages for implantable biosensor application. The very initial research found that noncovalently functionalzed CNTs could detect serum

proteins, including disease markers, autoantibodies, and antibodies. (Chen, et al. 2003) High-density nanotube device microarrays have been synthesized and fabricated for proteomics applications, aimed at detecting large numbers of different proteins inva multiplex fashion by using purely electrical transducers. These arrays are attractive because no labelling is required and all aspects of the assay can be carried out in solution phase. The bionanomultilayer biosensor of CNTs and horseradish peroxidase was prepared by layer-by-layer assembly and can be successfully applied to detect hydrogen peroxide, which presented a linear response for hydrogen peroxide from 0.4 to 12.0 μM with a detection limit of 0.08 μM. The MWNTs in the biosensor provided a suitable microenvironment to retain HRP activity and acted as a transducer for improving the electron transfer and amplifying the electrochemical signal of the product of the enzymatic reaction exhibited a fast, sensitive and stable response. (Liu, et al. 2008) DNA aptamer is highly selective and has been used as molecular recognition elements to functionalize CNT preparing filed effect transistor, which has shown high effect detecting two important enzymes elastase and thrombin. The lowest detection limit of the sensor used in their work is around 10 nM. For the selective absorption of DNA on to CNT surface, the supramolecular structure of DNA and CNT could be made used for sensing DNA by it modified CNT electronic properties. The developed fully electronic DNA sensors based on CNT field effect devices has achieved and found to be a effective approach for further understanding of DNA/CNT interaction mechanism. (Tang, et al. 2006)

An important composite biosensor is based on Chitosan/CNT. Chitosan is the only cationic biopolymer. For the solution sensitivity of positive charged amino groups in the chitosan molecular chain, it has variety important biological functions in tissue engineering, immune and drug delivery. (Rinaudo, et al. 2006) Chitosan/CNT composite material has been found to be of good biocompatibility for neutral cells growth. (Thompson, et al. 2009) Their suspension coated on glass carbon substrate could detect NaDH in a fast response time ($t_{90\%}$<5 s). The susceptibility of chitosan to chemical modifications has been made used for covalently immobilizing glucose dehydrogenase (GDH) in the chitosan/CNT films using glutaric dialdehyde (GDI). The stability and sensitivity of the GC/CNT/Chitosan/GDI/GDH biosensor allowed for the interference-free determination of glucose in the physiological matrix (urine). In pH 7.40 phosphate buffer solutions, linear least-squares calibration plots over the range 5-300 μM glucose (10 points) had slopes 80 mA $M^{-1}cm^{-2}$ and correlation coefficient 0.996. Its detection limit was 3 μM glucose. (Zhang, et al. 2004) A composite of MWCNTs-chitosan was used as a matrix for entrapment of lactate dehydrogenase onto a glassy carbon electrode in order to fabricate amperometric biosensor. (Tsai, et al. 2007) CNT-chitosan-lactate dehydrogenase nanobiocomposite film exhibits the abilities to raise the current responses, to decrease the electrooxidation potential of β-nicotinamide adenine dinucleotide and to prevent the electrode surface fouling. The optimized biosensor for the determination of lactate shows a sensitivity of 0.0083 A M^{-1} cm^{-2} and a response time of about 3 s. The proposed biosensor retained 65% of its original response after 7 days. The immobilization of acetylcholinesterase (AChE) on CNTs/chitosan composite was also proposed. (Du, et al. 2007) Based on the inhibition of organophosphorous insecticide to the enzymatic activity of AChE, using triazophos as a model compound, the conditions for detection of the insecticide were explored. The inhibition of triazophos was proportional to its concentration in two ranges, from 0.03 to 7.8 μM and 7.8 to 32 μM with a detection limit of 0.01 μM. A 95% reactivation of the inhibited AChE could be regenerated for using pralidoxime iodide within 8 min. The

constructed biosensor processing prominent characteristics and performance such as good precision and reproducibility, acceptable stability and accuracy, fast response and low detection limit has potential application in the characterization of enzyme inhibitors and detection of toxic compounds against to enzyme.

9. Biopolymer/CNT composite actuator

Biopolymer/CNT composite actuators were initially found to play important role for smart drug delivery. A novel gelatin-CNTs hybrid hydrogel was synthesized. [Li, December 2003] Cooperation with CNT could maintain the stability of the hybrid hydrogel without cross-linking at 37.8 ^{o}C. It have also been noticed that the novel hybrid hydrogel with or without crosslinking can be used in protein separating. Silk fibroin in the sol state can interact with nanotubes through hydrophobic interactions. (Kim, et al. 2009) The pH-sensitive properties of the CNTs dispersed with silk fibroin has been investigated and believed to have potential value for the preparation of novel biomaterials for cancer detection and treatment. Composite gel of chitosan/CNT has also been found to be of improved actuation performance under pH and electrical field stimulation. (Ozarkar, et al. 2008) Modulated release of dexamethasone from their composite has been show to be faster than traditional method (Naficy, et al. 2009). Electrochemical investigation has shown that the chitosan/CNT composite electrodes can foster prolific L929 cell growth and stimulate the cells growth. (Whitten, et al. 2007; Lynam, et al. 2009) In the history of piezoelectric material development, the first discovered piezoelectric polymer is biopolymer cellulose by testing the piezoelectricity of wood. (Fukada, et al. 1955) Lately, the piezoelectricity has also been found in the invertebrate exoskeletons, including crap shell, and bone. (Zilberstein, et al. 1972; Yamashiro, et al. 1989; Fukuda, et al. 1957) Molecular level research approved that the those piezoelectricity comes from biopolymers such chitin, collagen, DNA, which reveals that piezoelectricity is a fundamental properties of biological tissues and may comes from the directed dipole of chemical bond in their ordered structure. (Fukada, 1964 &1975; Ando, 1976; Shamos, 1967). A recent study also show that CNT could reinforce the piezoelectric actuation performance of regenerated cellulose while the reinforced crystalline is in agreement with it. (Yun, et al. 2007) For the structure of biopolymer near CNT surface is directed, single units of biopolymer/CNT at nanoscale could be obtained, which could be further developed as important electromechanical actuator and sensor as nano-electro-mechanical-system for implant biomedical devices. As has been mentioned above, chitosan is a mutifuctional biopolymer involved in variety of biological tissues' formation and functions. It has been widely studied not only as sensor but also actuator for variety of usages.

Because chitosan is a very effective agent for stabilization of CNTs, we have initially constructed a high speed, highly stable, full solid chitosan/CNT bimorph electrochemical composite actuator. (Lu, & Chen, 2010) For the high weight fraction of CNTs in uniform chitosan/CNT composite electrode, the conductivity of composite electrode could reach as high as 34.25 S.cm^{-1}, which was made use for reinforcing the electrochemical charging and discharging ability of bimorph structure, as illustrated in figure 8. The bending actuation performance of 15mm long composite strip show 2 mm/s high speed actuation performance under a 3 V low voltage stimulation. This performance is higher than most of traditional IPMC actuator strip while no heavy metal element is needed, which is important for biomedical and harptic interface applications.

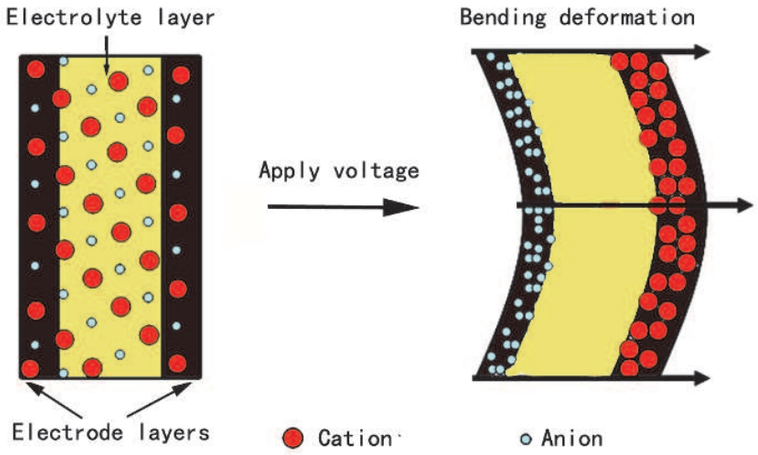


Fig. 8. Schematic illustration for the bending actuation mechanism of bimorph CNT composite, the applied voltage redistribute the cations and anions from the raw state (left) to a new balanced state (right).

CNTs are of excellent electrical conductivity, thermal stability and conductivity. Their temperature could be periodically changed in wide frequency range by electrothermal energy transition under periodical electrical current control. CNTs temperature waving leads to the countering temperature waving of a very thin gas layer surrounded them, which can be achieved by the high frequency range thermal variation of CNTs for the low thermal conductivity of gas induced thermal energy accumulation in very short time. In the thermal actuation system, the periodical thermal accumulation induced equivalent adiabatic expansion and shrinkage of surrounded thin layer gas medium. This character gives birth to the nanoscale loudspeaker. (Xiao, et al. 2008) On realized that by replacing gas medium with chitosan that helically wrapped on CNTs, we could obtain an electrothermal stimulated macroscopic composite actuator. The electrothermal actuation performance of chitosan/CNT composite has thus been detailed studied (Hu, et al. 2010). Biopolymer chitosan functionalized CNTs uniformly distributed as a network in bulk material reversible actuating polymer matrix in the frequency lower than 10 Hz, which is close to organisms' behaviors. The cyclic test shows that the reversible electrothermal actuation could be achieved for more than 3 thousand times. It is believed to be of great value for not only high sensitivity engineering actuation materials but also electrical current controllable drug release system that attached to skin.

10. Conclusion

In summary, the latest ten year progress on key topics for CNT engineering assisted by biopolymers has been reviewed. The dispersion, purification and specific chiral separation for CNTs assisted by biopolymers have been successful achieved. Moreover, their cooperation broaden the application range of CNTs into biomedical fields especially drug delivery and tissue engineering. The cooperation of biopolymers with CNTs provides impresive sensing and actuation performances that traditional materials can't reach. Varieties of technologies for biopolymer assisted CNTs engineering have been developed and thus belived to be of great potential for further applications.

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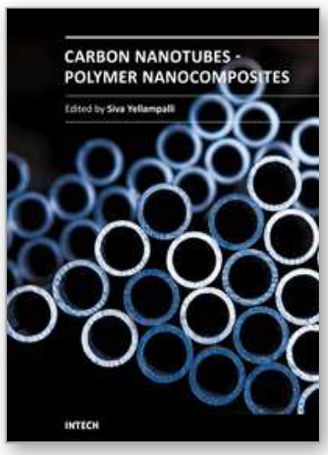

Carbon Nanotubes - Polymer Nanocomposites

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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This books focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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