

Recent Advances in Bio-Sourced Polymeric Carbohydrate/Nanotube Composites

Dagang Liu,¹ Ying Zhang,¹ Xun Sun,¹ Peter R. Chang^{2,3}

¹Department of Chemistry, Nanjing University of Information Science and Technology, Nanjing 210044, China

²BioProducts and BioProcesses National Science Program, Agriculture and Agri-Food Canada, Saskatoon, SK, S7N0X2, Canada

³Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, S7N 5A9, Canada

Correspondence to: D. Liu (E-mail: dagangliu@gmail.com) or (dagang@nuist.edu.cn) and P. R. Chang (E-mail: peter.chang@agr.gc.ca)

ABSTRACT: Nanotubes (NTs), especially carbon nanotubes (CNTs), have attracted much attention in recent years because of their large specific surface area, and their outstanding mechanical, thermal, and electrical properties. In this review we emphasize the development of fascinating properties of polymeric carbohydrate/CNT composites, particularly in terms of their mechanical and conductivity properties and potential applications. Many methods used to modify CNTs during preparation of polymeric carbohydrate/CNT composites are presented. Moreover, we also discuss the enhanced mechanical and electrical effectiveness when hybrid CNTs or halloysite nanotubes were incorporated into different carbohydrate polymer matrices. Finally, we give a future outlook for the development of polymeric carbohydrate/CNT composites as potential alternative materials for various applications including sensors, electroactive paper, electrodes, sorbents for environmental remediation, packaging film, specialty textile, and biomedical devices.

© 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40359.

KEYWORDS: biopolymers and renewable polymers; nanotubes; graphene and fullerenes; composites

Received 15 November 2013; accepted 29 December 2013

DOI: 10.1002/app.40359

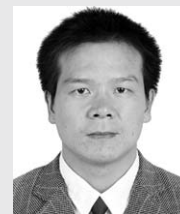
INTRODUCTION

A nanotube (NT) is a general term for a tube-like structure and may refer to nanotubes (NTs) made from carbon, silicon, halloysite (HNTs), titanate, DNA, etc. Carbon nanotubes (CNTs) are cylindrical graphite hollow tubes with one or more concentric layered cylindrical shells of graphene sheets. CNTs are classified as single-walled (SWCNTs), double-walled (DWCNTs), or multiwalled (MWCNTs) according to the cylinders of graphene sheets. CNTs have demonstrated remarkable structure-properties that allow a number of exciting potential applications. CNTs have proven to be excellent sorbents for many pollutants¹ and are effective reinforcement fillers at very low loading levels due to their large specific surface area, small structure, extremely high mechanical strength, and high chemical stability. CNTs also have unique electrical and thermal properties leading to a wide variety of possible applications in the fields of electrochemical and electronic devices, fuel cells, and sensors and probes.² CNTs also have the ability to promote electron-transfer reactions when used as electrode materials. Interestingly, sensors based on CNTs have improved the voltammetric response (lower over-voltages and higher peak currents) of a variety of clinical, biological, and environmental compounds.³

HNTs are a type of one-dimensional layered aluminosilicate with a molecular formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ which presents a hollow nanotubular structure with an aspect ratio of about 20. HNTs belong to the kaolin group of minerals mined from natural deposits. The chemical properties of HNT's outermost surface are similar to those of SiO_2 , while the properties of the inner cylinder core are similar to those of Al_2O_3 . Because of their unique nanoscale tubular, rod-like structure and chemical activity, HNTs have applications in many fields such as in bioreactors, time-release capsules, catalysts of polymer degradation, templates, reinforcement nanofillers, and high-tech ceramic applications. Moreover, HNTs show good compatibility with chitin or chitosan, and can thus be incorporated into chitin or chitosan nanocomposites or hybrid materials.⁴

Inorganic CNTs or HNTs however still have some problems, e.g., low processability because of their low molecular weight and less flexible properties. To overcome these problems, NTs are incorporated into polymeric matrices (such as carbohydrate polymers) to gain improved properties and extend their application in different fields including flexible electrodes in displays, electronic paper, antistatic coatings, bullet-proof vests, protective clothing, high-performance composites for aircraft and automotive industries,⁵ and biomedical devices.⁶ Carbohydrate

Dr Dagang Liu is a full professor at the Nanjing University of Information Science & Technology. He was awarded a Ph.D. in Polymer Physics & Chemistry on natural polymers. He currently studies environmental friendly nano or nanocomposite materials based on natural polymers, as well as their application in environmental treatment and sensing. Dr. Liu has published more than 40 peer-reviewed papers, 4 book chapters, and 6 patents (granted).



Dr. Chang works as a Research Scientist with Agriculture and Agri-Food Canada. He is also affiliated with the Department of Chemical and Biological Engineering, University of Saskatchewan as an Adjunct Professor. His research interests focus on "Developing new opportunities for agriculture from bioresources". He works on the isolation, fractionation, concentration, purification, conversion, transformation, modification, characterization, and processing of biopolymers from biomass and grain into biocomposites, nanocomposites, bioplastics, biomaterials, ecomaterials, biofuels, fine chemicals, and other industrial products. Prior to joining the Government of Canada and University of Saskatchewan undertaking a research-oriented programme with medium and long-term objectives, Dr. Chang worked (15 years) for several consulting firms which offered practical solutions to domestic and international companies in the agri-food industries. He has published 114⁺ peer-reviewed papers, 90⁺ technical/confidential reports to industry, 6 book chapters, and 4 patents (granted).



polymers have been exploited in industrial applications such as food, textiles, paper, wood, adhesives, biodegradables, biorefining, pharmaceuticals, and materials. In particular, polymeric carbohydrate/nanotube composites have been developed extremely rapidly in recent years. Polymeric carbohydrate/nanotube composites have wide applications because they possess both the extraordinary (electrical, mechanical, and adsorption) properties of CNTs and the specified functionality derived from polymeric carbohydrates. In this review we examine some common practices for preparation and structure of carbohydrate polymer/nanotube composites as well as the effects of nanotubes on the properties of the polymeric carbohydrate matrices. We also give a future outlook for the development of polymeric carbohydrate/nanotube composites as potential alternative materials for various applications.

FABRICATION OF POLYMERIC CARBOHYDRATE/NANOTUBE COMPOSITES

Main strategies for the fabrication of carbohydrate polymer/nanotube composites include solution or melt processing of composites, graft polymerization, electrospinning, coagulation spinning for composite fibers and yarn production, and layer-by-layer (LBL) assembly. Dispersion of the nanotubes plays a key role in elevating the properties and changing the structure of nanocomposites. CNTs without polar surfaces usually do not have good interfacial compatibility with the hydrophilic carbohydrate matrix. To improve compatibility between CNTs and polymeric carbohydrates three methods are commonly used: (1) Acid-treatment of CNTs to facilitate the formation of hydrogen-bonds with chitosan chains and thus improve interfacial compatibility between the chitosan matrix and nanotubes; (2) LBL

assembly of polymeric carbohydrate and acid-treated CNTs; and (3) introduction of covalent linkages to the CNT/carbohydrate polymers. In addition, the use of surfactant-like sodium dodecyl sulfate (SDS)-coated CNT was also a good method for achieving reproducible nanotube dispersions and obtaining a stable homogeneous solution.⁷ HNT is a polar inorganic filler full of ionic groups which allow it to directly mix with polymeric carbohydrates without any modification.

Cellulose and its Nanotube Composites

Cellulose is a carbohydrate consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units.⁸ Cellulose is an important structural component in the primary cell wall of green plants, many forms of algae, and oomycetes. Some species of bacteria secrete cellulose to form biofilms.⁹ Unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighboring chain, holding the chains firmly together side-by-side, and forming microfibrils with high tensile strength. Several different crystalline structures of cellulose are known that correspond to the location of the hydrogen bonds both between and within strands.¹⁰ Properties of cellulose greatly depend on chain length or degree of polymerization.

Regenerated Cellulose/CNT. Regenerated cellulose (RC) can be prepared by dissolving pulp in solvents such as LiCl/*N,N*-dimethylacetamide, *N*-methylmorpholine-*N*-oxide (NMMO), sodium hydrate/urea, or ionic liquid.¹¹ NMMO monohydrate is a good dispersing agent for acid-treated SWNT and a solvent for cellulose. Thus, acid-treated SWNTs were well dispersed in the nanocomposite film and played an important role in improving the

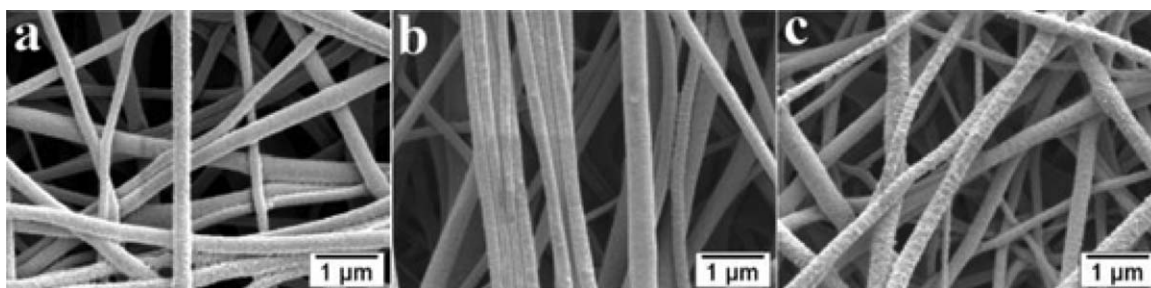


Figure 1. SEM images showing the surface morphologies: (a) cellulose, (b) 0.11 wt % MWCNT/cellulose, and (c) 0.55 wt % MWCNT/cellulose fibers.¹⁸

mechanical properties, thermal properties, and electric conductivity of nanocomposite films.¹² MWCNTs were covalently grafted to cellulose by reacting imidazolid-MWCNTs with cellulose solution. In addition, well-aligned bundles of MWCNTs in stretched MWCNTs/cellulose paper (with stretching ratio = 1.8) were covalently grafted to cellulose chains.¹³ The room temperature ionic liquid 1-butyl-3-methylimidazolium acetate ([bmim][OAc]) was chosen as an intermediary solvent to improve the homogeneity of cellulose-SWNT composites. Results showed that cellulose/SWNT exhibited a less tangled tissue instead of crowded bundles, demonstrating that the introduction of cellulose molecules efficiently promoted the dispersal of SWNTs.¹⁴ Furthermore, *N,N*-carbonyldiimidazole and ethyl methyl imidazolium acetate were also reported to be effective at increasing the dispersion of CNTs in cellulose solution.^{6,15} Cellulose/MWCNTs in ethyl methyl imidazolium acetate can be effectively used for solution spinning of composite fibers with enhanced tensile strength, reduced thermal shrinkage, and good electrical conductivity.

Bacterial Cellulose/CNT. LBL assembly is a simple, versatile, and relatively inexpensive means of providing multifunctional molecular assemblies of tailored architectures and material properties for various versatile reaction/sensing materials of

nanometer thickness and will enable large-scale, reproducible production of smart functional materials. By this means, snow-like bacterial cellulose (BC) assemblies were synthesized in an agitated culture, whereas fibrous and rice-like BC assemblies are produced in the presence of MWCNTs in an agitated culture.¹⁶ The gradual dispersion of MWCNTs along the radial direction indicates that BC assemblies LBL with increasing culture time.

Cellulose Derivatives/CNT. The melt-compounding method was used to prepare cellulose acetate (CA)-based nanocomposites with various contents of neat MWCNT or acid-treated MWCNT due to the fact that CA is much more stable and processable than its counterpart, pure cellulose.¹⁷ MWCNT-loaded CA solutions were electrospun into ultrafine and uniform composite fibers with 257 and 228 nm for those with 0.11 and 0.55 wt % MWCNTs, respectively. High-resolution SEM images shown in Figure 1 reveal the surface roughness induced by the deacetylation process. In the MWCNT/CA 3D fibrous mats no protrusion of MWCNTs and no free MWCNTs were observed [Figure 1(b,c)] indicating the successful inclusion of MWCNTs in the CA fiber matrix.¹⁸ In addition, an efficient strategy consisting of cutting, chain extension, introduction of active groups, and homogeneous reaction tactics was employed

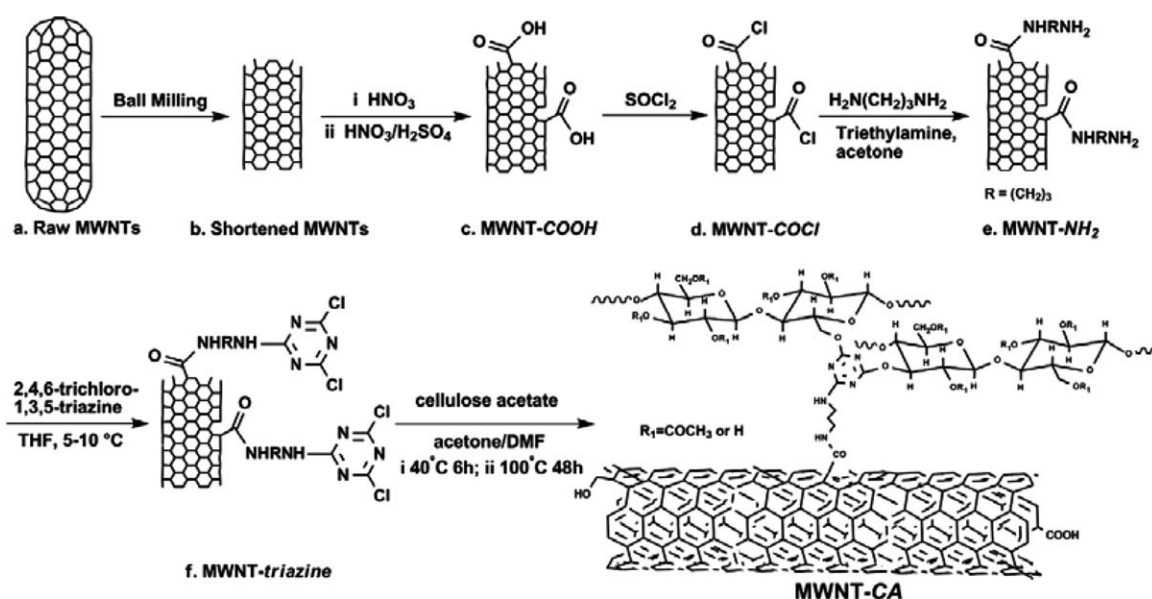


Figure 2. Functionalization of MWCNTs (also called MWNTs) with cellulose acetate.¹⁹

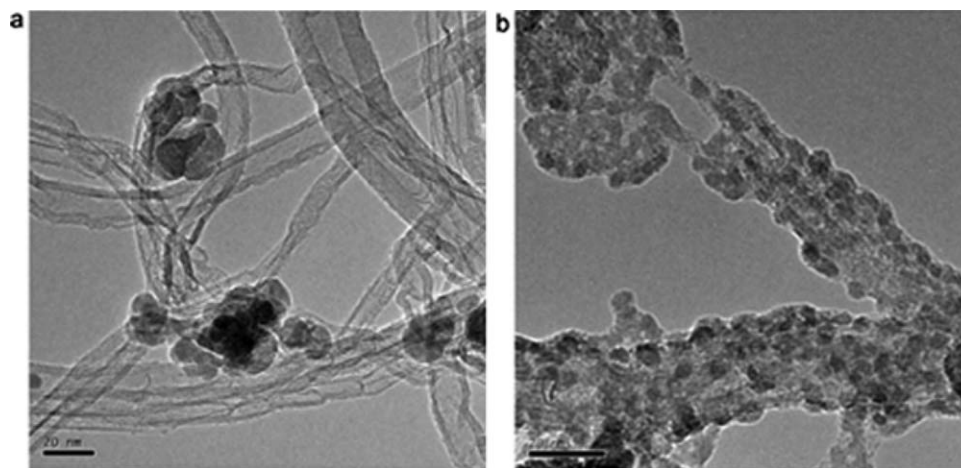


Figure 3. TEM micrographs of MWCNT/iron oxide (a) and MWCNT/starch/iron oxide (b).²⁴

to functionalize MWCNTs with CA. Introduction of amino groups from modifier 1, 3-propanediamine was vital way to prepare functional MWCNTs with sufficient active groups (Figure 2). And then 2, 4, 6-trichloro-1, 3, 5-triazine, a compound containing three chlorine atoms with different reactivities, was used as a good reactive intermediate to bridge MWCNTs and CA. It was verified that reaction between chloride atoms in the MWNT-triazine and hydroxyl groups in the CA had contributed to the formation of MWNT-CA conjugates.¹⁹

Starch and its Nanotube Composites

Starch is the most common polymeric carbohydrate in the human diet and is contained in large amounts in staple foods such as potatoes, wheat, corn, pulses, rice, and cassava. Starch molecules arrange themselves in the plant in semicrystalline granules. Each plant species has a unique starch granular size: rice starch is relatively small (ca. 2 μm) while potato starches have larger granules (up to 100 μm). Starch consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20–25% amylose and 75–80% amylopectin by weight.²⁰ Industrial nonfood uses of starch include use in adhesives, garments, plastics, thickening agents, and stiffening agents.

Soluble Starch/CNT Composites. Starch becomes soluble in water when it is heated and the semicrystalline structure is lost allowing the smaller amylose molecules to leach out of the granule to form a network that retains water and increases the mixture's viscosity. During cooling or prolonged storage of the paste the semicrystalline structure partially recovers. Soluble starch based nanocomposites containing very low loading levels of MWCNTs (0.027 wt % and 0.055 wt %) were developed by wrapping the MWCNTs with a starch-iodine complex. These materials exhibited greatly improved tensile and impact properties as a consequence of well-dispersed nanotubes in the matrix and strong adhesion between the phases.²¹ When soluble starch was grafted to carboxylated MWCNTs (CMWCNTs) to disperse the CNTs in either water or the polysaccharide films the surface of the CNT was smooth, while CMWCNTs covered with the grafted starch were rough. There was no gap visible between starch and CMWCNTs when observed by TEM.²²

Plasticized Starch/CNT Composites. Starch can be processed into thermoplastic with a certain amount of plasticizer by casting it from solution, by extruding it between two nip rollers, or by thermal compress-molding. The flexibility and processability of starch can be improved by promoting the mobility of the molecular segment by the addition of plasticizers, like water, polyols (propylene glycol, triethylene glycol, ethylene glycol, and butane diols), sugars, etc.; however, the tensile strength and modulus decrease sharply. Functionalized MWCNTs were proven to be an effective filler for the reinforcement of plasticized starch films.²³ The TEM micrographs in Figure 3 show the morphologies of MWCNT/iron oxide and MWCNT/starch/iron oxide. Figure 3(a) depicts an entangled network of acidified MWCNTs, on which clusters of iron oxides are hanged. In Figure 3(b), MWCNTs are covered with the starch component in which iron oxide nanoparticles were uniformly dispersed without obvious aggregation. The starch component grafted on the surface of the MWCNT was not destroyed in the process of loading iron oxides. The size (ca. 7 nm) of iron oxide nanoparticles in MWCNT/starch/iron oxide was smaller than those in MWCNT/iron oxide (ca. 20 nm).²⁴

Multicomponent Starch/CNT Composites. Functionalized MWCNT reinforced polyacrylonitrile-*co*-starch nanocomposites were prepared using an *in situ* polymerization technique. MWCNTs were functionalized by acid treatment followed by sonication and dispersion in PAN-*co*-starch copolymer. The PAN-*co*-starch/MWCNT nanocomposites that were synthesized had high performance in thermal stability, tensile, and electrical properties. The electrical percolation threshold of PAN-*co*-starch/MWCNT nanocomposites was attained at 1 wt %, which is much lower than conventional composites.²⁵

Chitin or Chitosan and Their Nanotube Composites

Chitin, poly (β -(1-4)-*N*-acetyl-D-glucosamine), is a main component of the cell walls of fungi, the exoskeletons of arthropods such as crustaceans (e.g., crabs, lobsters, and shrimps) and insects, the radulas of mollusks, and the beaks and internal shells of cephalopods, including squid and octopuses. Chitin occurs in nature as ordered crystalline microfibrils that form structural components, serving many functions where reinforcement and strength are

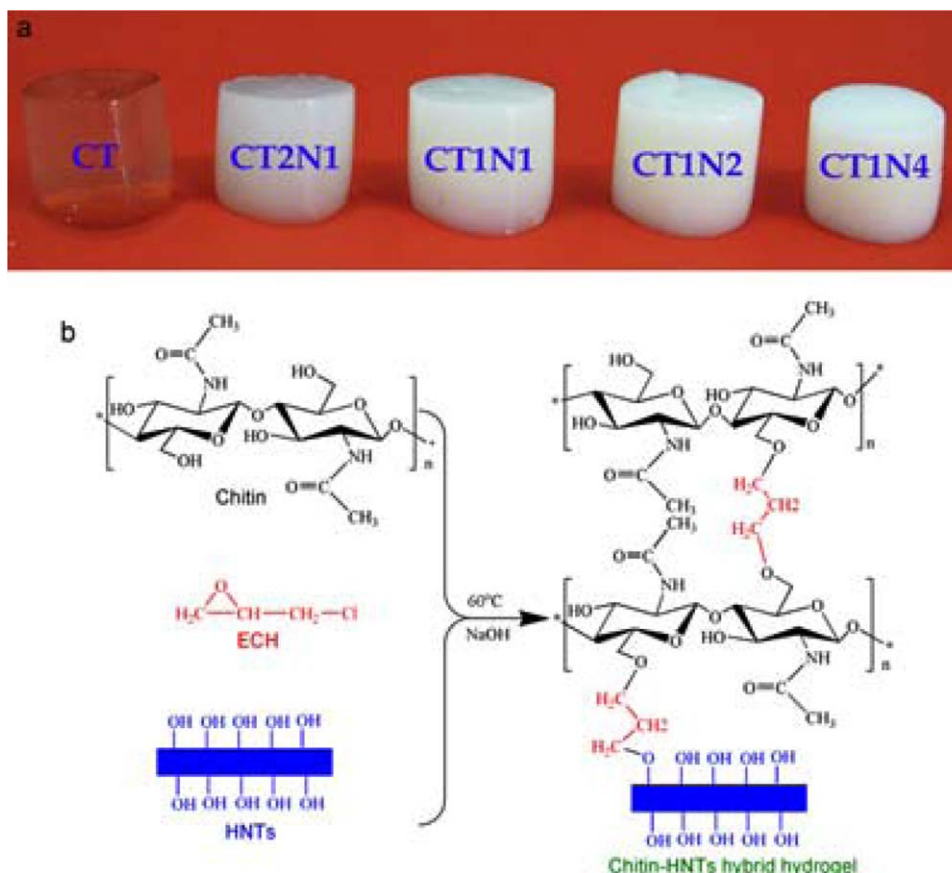


Figure 4. Appearance (a) and reaction mechanism (b) of chitin and chitin/HNTs hybrid hydrogel.⁴ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

required.²⁶ Chitin has also proven useful for several medical and industrial purposes, such as a flocculating agent, a wound healing agent, a sizing and strengthening agent for paper, and a delivery vehicle for pharmaceuticals and genes, due to its biodegradable, renewable, antibacterial, and fungistatic properties.

When the degree of deacetylation of chitin reaches more than 50%, it becomes soluble in aqueous acidic media and is called chitosan. In other words, chitosan is a linear polysaccharide composed of randomly distributed β -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Solubilization occurs by protonation of the -NH_2 groups on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media. The advantage of chitosan over other polysaccharides (cellulose, starch, galactomannans, etc.) is that its chemical structure allows specific modifications without too many difficulties at the C-2 position. Specific groups can be introduced to design polymers for selected applications.²⁶ Chitosan is an excellent adsorbent for the removal of organic pollutants (such as medicines, proteins, dyes, etc.) due to its high content of hydroxyl and amino groups in the polymer chains, which can form hydrogen bonds with many organic compounds.¹ Chitosan displays nontoxicity and biocompatibility, is susceptible to chemical modification, and is inexpensive; therefore, it has been widely used in medicine, drug delivery, water treatment,

membranes, hydrogel carriers of drugs for controlled release, tissue engineering, and immobilization matrices for biosensors and bioreactors.^{27,28} Commonly, there are several methods of functionalizing CNTs with CS: LBL self-assembly, wet spinning, electrochemical deposition, surface-deposition, crosslinking, and covalent grafting.

Chitin or Chitosan/Nanotube Hybrid Hydrogels. Chitin was dissolved in an aqueous NaOH/urea solution and then mixed with HNTs to prepare hybrid hydrogels via crosslinking with epichlorohydrin.⁴ Scanning electron microscopy of the hybrid hydrogels showed highly porous microstructures. Figure 4 shows the appearance and reaction mechanism of chitin and chitin/HNTs hybrid hydrogel. The prepared pure chitin hydrogel was transparent, while all chitin/HNTs hybrid hydrogels were opaque [Figure 4(a)]. This may be due to the relatively large dimension of HNTs compared to the visible light wavelength. Figure 4(b) illustrates the crosslinking reaction mechanism of the chitin-HNTs hybrid hydrogels. Epichlorohydrin is a highly efficient cross-linking agent both for chitin and HNTs that forms covalent ether bridges between OH groups of the chitin chains as well as the hydroxyl groups located on the HNTs sheets, particularly on their edges.

Chitin or Chitosan/Nanotubes Hybrid Films. Naturally occurring HNTs were incorporated and uniformly dispersed into

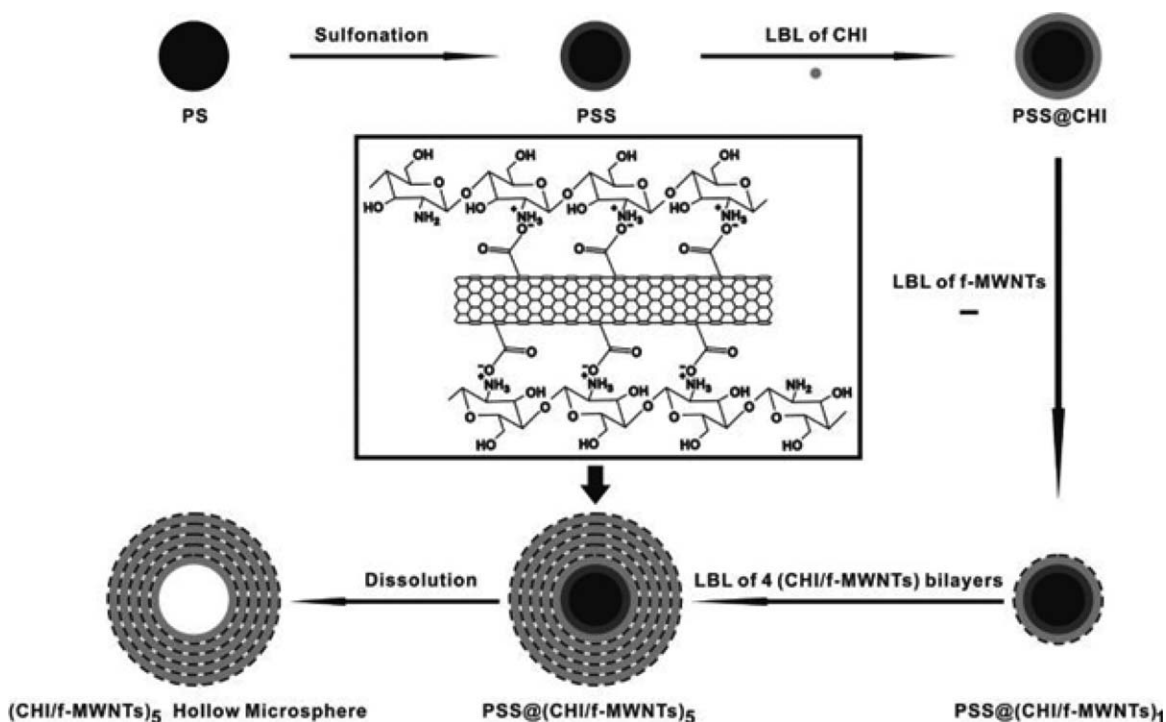


Figure 5. Scheme for preparation of CHI/f-MWNT hollow microspheres.³¹

chitosan to form bionanocomposite films via solution casting. The electrostatic attraction and hydrogen bonding interactions between HNTs and chitosan resulted in enhanced properties and changed microstructure.²⁹ Addition of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) was helpful for improving the dispersion of MWCNTs and the interfacial compatibility between MWCNTs and chitosan.³⁰

Chitin or Chitosan Hybrid Microspheres. Multilayer hollow microspheres were fabricated via LBL assembly using electrostatic interaction between the polycation chitosan and the anion carboxyl-functionalized MWNTs on polystyrene sulfonate microsphere templates.³¹ Figure 5 shows the preparation of hollow microspheres from chitosan/MWNTs (also called chitosan/MWCNTs). In step 1, the uniform polystyrene particle previously prepared by dispersion polymerization was sulfonated in concentrated sulfuric acid to obtain the polystyrene sulfonate particle used as a template. In step 2, chitosan was deposited on the polystyrene sulfonate template to positively charge the

surface. In step 3, a layer of negatively charged MWNTs was deposited. In step 4, the bilayers of chitosan and MWNTs were alternately assembled in the desired cycles. In the last step, the polystyrene sulfonate template was removed by dissolution yielding the hollow microsphere.³¹

Alginate and its Nanotube Composites

Alginates are linear unbranched polymers containing β -(1,4)-linked D-mannuronic acid (M) and α -(1,4)-linked L-guluronic acid (G) residues. Although these residues are epimers (M residues being enzymatically converted to G after polymerization) and only differ at C5, they possess very different conformations; M being ⁴C₁ with diequatorial links between them and G being ¹C₄ with diaxial links between them.³² Alternating poly α -(1,4)-linked L-guluronate- β -(1,4)-linked D-mannuronate contains both equatorial-axial and axial-equatorial links and takes up dissimilar rather disorderly conformations. There are hydrogen bonds between the carboxyl group on the mannuronate and the 2-OH and 3-OH groups of the subsequent guluronate, but the different degrees of freedom of the two

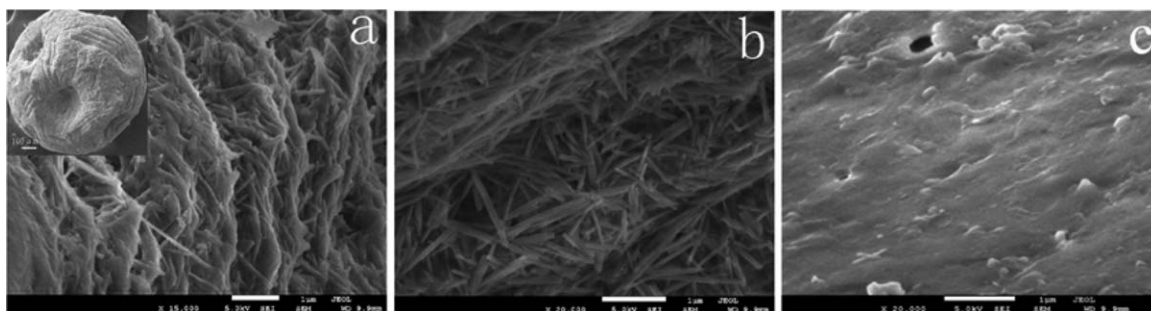


Figure 6. SEM images of the external surface (a) and the internal structure (b) of alginate/HNT hybrid beads; and the external surface (c) of the pure alginate beads.³⁹

residues gives them greater overall flexibility than the poly β -(1,4)-linked D-mannuronate chains. The free carboxylic acids (without counter ion) have a water molecule H_3O^+ firmly hydrogen bound to carboxylate (pK_a M 3.38, pK_a G 3.65).

Calcium, sodium, and ammonium alginates have been used in foam, cloth, and gauze for absorbent surgical dressings. These gels can be heat treated without melting, although they may eventually degrade. Alginate's solubility and water-holding capacity depend on pH (precipitating below about pH 3.5), molecular weight (lower molecular weight calcium alginate chains with <500 residues showing increased water binding with increasing size), ionic strength (low ionic strength increases the extended nature of the chains) and the nature of the ions present.³³

Carbon nanotubes coated with alginate through noncovalent functionalization have been shown to be soluble and disperse in water. Results reveal that alginate can wrap around SWCNT by virtue of van der Waals attractions and organize into a compact helical structure, a process induced in the gas phase by hydrogen-bond interactions. Alginate can solubilize and efficiently disperse MWCNTs in water, as was observed for amylose wrapping around SWCNT.³⁴

Alginate/Nanotube Hybrid Hydrogels. Alginate hydrogels successfully reinforced with SWCNTs were prepared using a free-form fabrication technique. Three dimensional hybrid alginate/SWCNT tissue scaffolds were then fabricated in a multinozzle biopolymer deposition system, which made it possible to disperse and align SWCNTs in the alginate matrix.³⁵

Alginate/Nanotube Hybrid Micro- or Nanofibers. A biosorbent of calcium alginate/MWCNT composite fiber was fabricated by wet spinning and cross-linking using $CaCl_2$. The composite fiber exhibited the excellent adsorption properties of both alginate and MWCNTs for heavy metals and dyes, and also prevented MWCNTs from breaking off the composites to cause secondary pollution/contamination in water.³⁶ In other work, adsorbent calcium alginate/MWCNT composite fibers were prepared by wet spinning and effectively used as environmentally friendly adsorbents for the removal of methyl orange (MO) from aqueous solution due to their efficient and fast adsorption process.³⁷ Nanofibers of alginate/CNT hybrid composite were prepared using a method of electrospinning out of aqueous solutions. Electron micrographs showed the CNTs were well incorporated along the nanofibers.³⁸

Alginate/Nanotube Hybrid Microsphere. Soluble alginates, such as those of sodium, potassium, or magnesium, form a viscous sol that can be changed into gel beads via chemical reaction with compounds such as calcium ions. As shown in Figure 6[(a), inset] the surface of the dried bead was rough and shriveled. The fine surface structure showed HNTs were immobilized by the alginate gel and formed a porous structure on the alginate/HNT hybrid bead surface, Figure 6(a). In Figure 6(b) it can be seen that the HNTs were loosely overlapped in the interior structure of the alginate/HNTs hybrid beads; however, the surface of the pure alginate bead was smooth and dense in Figure 6(c).³⁹ Polymer-assisted dispersal of CNT into the cross-linked alginate capsules has potential in biomedical applications

Table I. Mechanical Properties of Polymeric Carbohydrate/CNT Hybrid Nanocomposites

Samples	Young's modulus (GPa)					Tensile strength (MPa)					Elongation at break (%)					References
	0	1	3	5	10	0	1	3	5	10	0	1	3	5	10	
CNT/cellulose	13.1	14.4	12.4	13.9	13.0	198	244	239	253	179	2.8	3.7	5.5	5.8	3.2	15
	3.1	2.7	2.9	2.6	80.6	71.4	75.7	59.4	75.7	59.4	6.1	9.5	8.2	8.2	5.9	42
CNT/chitosan	0	0.1	0.5	1.0	2.0	0	0.1	0.5	1.0	2.0	0	0.1	0.5	1.0	2.0	^a
	0.6	1.3	2.3	2.5	11.6	14.5	18.4	25.4	25.4	25.4	2.0	2.9	3.9	5.0	5.0	46
CNT/starch	1.1	2.2	37.7	2.2	37.7	74.3	49.5	13.4	47	47	47	47	47	47	47	47
	2.0	2.4	3.24	3.9	4.4	39.6	50.6	76.3	98.3	102.8	15.2	14.1	13.3	11.3	7.9	48
CNT/starch	3.1	3.5	4.1	4.1	72.0	10.7	11.4	36	42	38	30	30	30	30	30	30
	0	0.5	1.0	2.0	3.0	0	0.5	1.0	2.0	3.0	0	0.5	1.0	2.0	3.0	^a
CNT/starch	2.9	3.5	4.1	4.3	4.7	20.7	24.8	27.8	31.5	39.2	29.7	37.2	42.0	38.3	32.0	43
	4.5	5.6	7.1	7.2	6.0	55	53	49.0	35.0	28.0	45	45	45	45	45	45
CNT/starch	0.2	0.19	0.22	0.23	4.7	5.4	6.1	6.8	6.8	6.8	42.0	44.0	44.0	44.0	44.0	44

^aRepresents the content of CNT (wt %).

as a drug carrier.⁴⁰ A mixture of DWCNTs and BSA was suspended homogeneously in alginate and then added dropwise into a calcium chloride solution to form biocomposite beads. These beads were an efficient support for biomaterial immobilization.⁴¹

EFFECTS OF NANOTUBES ON THE PROPERTIES OF COMPOSITES

CNTs are considered to be the ideal reinforcing nanofiller for polymer matrices because of their unique mechanical properties, thermal stability, high aspect ratio, and electrical conductivity.

Reinforcement Effects

CNTs have an amazing combination of excellent electronic and mechanical properties, which has drawn the attention of scientists and engineers in a range of areas. Qi et al. found that regenerated cellulose (RC) film had a high mechanical strength and Young's modulus, with values of 80.6 MPa and 3.1 GPa, respectively. There was no obvious increase in the tensile strength, and even a slight decrease in the Young's modulus with the loading of CNT in CNT/cellulose films (Table I). However, the strain-to-failure was 11.1%, which is almost two times higher than that of the RC film (6.1%, shown in Table I).⁴² MWCNT/cellulose composite fibers were processed from solutions in ethyl methylimidazolium acetate (EMIAc) by Rahatekar et al. They found that a moderate enhancement of tensile strength was observed with a MWCNTs mass fraction of up to 0.05. A further increase in the nanotube content (0.07 wt %) did not result in further enhancement of tensile strength, and in fact it decreased when the mass fraction of MWCNTs was 0.1. No appreciable difference in tensile modulus was observed between the cellulose control and the composite fibers, while the strain to failure at 0.05 mass fraction MWCNT was 100% higher than that for the control cellulose fiber.¹⁵ The enhanced mechanical properties of these fibers could be mainly ascribed to the uniform dispersion and alignment of the MWCNTs within the cellulose matrix. It is well-known that the EMIAc-treated MWCNTs have hydrophilic groups, including carboxylic and hydroxyl groups, and, as a hydrophilic biopolymer, cellulose has three hydroxyl groups in each anhydroglucose unit. Therefore, it can be expected that some interactions, such as hydrogen bonding, will occur between cellulose and the MWCNTs. The compatibility and strong interaction between the MWCNTs and the cellulose greatly enhance the dispersion, as well as the interfacial adhesion, and thus significantly improve the mechanical properties of the cellulose matrix.

Reinforcement effects have also been found in the matrices of thermoplastic starch. Cao et al. found that the tensile strength and Young's modulus increased significantly (from 2.85 to 4.73 MPa and from 20.74 to 39.18 MPa, respectively) with an increase in MWCNT content from 0 to 3.0 wt %. The maximum value reached was 41.99% for the sample with 1.0 wt % MWCNTs.⁴³ Ma et al. found that the tensile strength and Young's modulus increased as the content of MWCNTs increased up to 4.75 wt%; however, the elongation at break decreased.⁴⁴ Liu et al. found that the addition of CMWCNTs significantly improved the tensile strength of the thermoplastic

starch (TPS) matrix as CMWCNT loading increased to 1.5 wt %, but was the reverse for elongation at break.⁴⁵ As the CMWCNT content increased to 1.5 wt %, the tensile strength of TPS/CMWCNT nanocomposites reached 7.7 MPa, while the pure TPS was only 4.5 MPa.⁴⁵ Ma et al.⁴⁴ showed an increase in both tensile strength and Young's modulus with increasing MWCNT content, and Cao et al.⁴³ showed a higher tensile strength and Young's modulus with the same mass fraction of MWCNTs. Liu et al.⁴⁵ showed the highest Young's modulus of all. In their study a facile solution dispersion method was used to prepare high performance thermoplastic starch (TPS)/CMWCNT nanocomposites. Because acid-treatment incorporated polar groups with the MWCNTs, the hydrophilicity of MWCNTs was improved and agglomerations of MWCNTs reduced. Therefore, CMWCNTs benefited greatly from the enhanced hydrogen-bonding interactions as well as the dispersion in TPS/CMWCNT nanocomposites, which resulted in improved mechanical performance of the TPS/CMWCNT nanocomposite films. However, CMWCNT content above 1.5 wt % caused deterioration of the plasticization of TPS, and also destroyed the continuity of the TPS matrix; therefore, TPS/CMWCNTs with higher CMWCNT contents (above 1.5 wt %) could have inferior mechanical properties.

Neat chitosan had a tensile strength of 11.6 MPa and a Young's modulus of 580 MPa, while the tensile strength and Young's modulus of chitosan loaded with 1.5% CNT were 30.4 MPa and 2815 MPa, respectively.⁴⁶ Both tensile strength and Young's modulus of the nanocomposites were greater than those of chitosan and increased by increasing the amount of poly(styrene sulfonic acid)-functionalized carbon nanotubes (CNT-PSSA) in the nanocomposites. Moreover, formation of nanocomposites with CNT also increased the elongation at break of chitosan from 2.0 to 6.1%. A small amount of water absorbed by the nanocomposite films may contribute to the increase in elongation. Wang et al. found that the addition of MWCNTs significantly improved the tensile properties of the chitosan matrix and that the mechanical properties increased with the increase in MWCNT loading levels. With only 0.4 wt % MWCNT filler, the tensile modulus and strength of the nanocomposite increased dramatically (by about 78 and 94%, respectively) as compared with those of its neat counterpart. As the loading level of MWCNTs increased to 0.8 wt %, the tensile modulus and strength of the chitosan/MWCNT composite were enhanced by about 93 and 99%, respectively.⁴⁷ Cao et al. found that the tensile strength and Young's modulus increased sharply from 39.6 to 102.8 MPa and from 2.01 to 4.35 GPa, respectively, with an increase in MWCNT loading level from 0 to 3.0 wt %. More specifically, the elongation at break of the nanocomposite film CS/MWCNTs-1.0 was 11.3%, which was a decrease of 25.6% in comparison to that of the neat CS film. In contrast, the tensile strength and Young's modulus were 98.3 MPa and 3.87 GPa, dramatic increases of 148 and 92%, respectively. However, when the MWCNT loading level was higher than 1.0 wt %, the tensile strength and Young's modulus increased slightly, but the elongation at break decreased from 11.3 to 5.6%.⁴⁸ Wu et al. found that the addition of MWCNTs significantly improved the tensile properties of the chitosan matrix, and the tensile strength and

Table II. Electrical Conductivity ($S\text{ cm}^{-1}$) of Polymeric Carbohydrate/CNT Hybrid Nanocomposites

	0.8 wt %	1.0 wt %	2.0 wt %	2.5 wt %	3.0 wt %	4.0 wt %	5.0 wt %	9.0 wt %	References
MWCNTs/ cellulose	7.0×10^{-6}	1.1×10^{-5}	6.0×10^{-5}		8.0×10^{-5}	1.0×10^{-4}	1.7×10^{-4}	3.1×10^{-3}	50
MWCNTs/ chitosan				0.005	0.15	0.21			51
PS/f- MWCNTs		1.38×10^{-9}	1.6×10^{-9}		1.69×10^{-9}				23

modulus increased with increasing MWCNT content. With the addition of only 0.1 wt % MWCNTs, the tensile strength and modulus of the nanocomposite increased dramatically, by about 50 and 16%, respectively. As the MWCNT content increased to 0.5 wt %, the tensile strength and modulus of the MWCNT/chitosan nanocomposite were enhanced by about 61 and 34%, respectively.³⁰

It has been generally recognized that the reinforcing efficiency of CNTs or HNTs depends strongly on their dispersion and orientation, as well as on the CNT/matrix interfacial strength.⁴⁹ Another critical issue is the impact of the shape of the embedded CNTs on the effective mechanical properties of the nanotube-reinforced polymer. The most effective approaches towards increasing the orientation of CNTs within a polymeric carbohydrate matrix include stretching and spinning (melt-spinning, solution-spinning, and electrospinning) the composites to form films and fibers. To achieve the full reinforcing potential of CNTs in polymers, they must be well dispersed and exhibit good interfacial strength with the matrix.

Enhanced Electrical Conductivity

CNTs are very effective fillers with a 1000 times higher current carrying capacity than copper wire,⁵⁰ which permits the movement of charge carried by the fillers through the matrix so the composite achieves a certain degree of electrical conductivity. The percolation threshold is characterized by a sharp jump in conductivity of many orders of magnitude which was attributed to the formation of a conductive network within the matrix. Thus, polymer/CNT composites show a very low percolation threshold for electrical conductivity because of the large aspect ratio and nanoscale dimension of nanotubes. The percolation threshold for electrical conductivity in polymer/CNT composites is also influenced by different nanotube characteristics such as aspect ratio, dispersion and alignment. Table II shows the values of electrical conductivity of polymeric carbohydrate/CNT hybrid composites. Kim and Park found that electrical conductivity increased as wt % increased. The conductivity levels were between 10^{-5} and 10^{-6} S cm^{-1} at wt % <1 and increased to 1.77×10^{-4} and $3.07 \times 10^{-3}\text{ S cm}^{-1}$ at 5 and 9 wt %, respectively.⁵¹ Piri et al. also found that with the increase in MWCNT content, the electrical conductivity increased; at 4 wt %, the electrical conductivity increased to 0.21 S cm^{-1} .⁵² Swain et al. found that the conductivity of the composite increased with the addition of very low concentrations (0.5–3 wt %) of functionalized MWCNT. The electrical conductivity increased gradually from 0.6×10^{-9} to $1.6 \times 10^{-9}\text{ S cm}^{-1}$ due to the addition of filler.²³ From these reported works, it is easy to determine that

the dispersion of nanotubes played a key role in improving the properties and changing the structure of nanocomposites, e.g., good dispersion of MWCNT will lead to good conductivity of the nanocomposites. CNTs without polar surfaces usually do not have good interfacial compatibility with the hydrophilic carbohydrate matrix.

Theoretically, noncovalent functionalization of nanotubes normally involves van der Waals, p-p, CH-p covalent bonds, or electrostatic interactions between the polymeric carbohydrate and the CNT surface. The advantage of noncovalent functionalization is that it does not alter the structure of the nanotubes and, therefore, both electrical and mechanical properties should also remain unchanged. There are several noncovalent approaches for nanotube functionalization such as surfactant-assisted dispersion, polymer wrapping, plasma polymerization-treatment, and polymerization filling technique (PFT).⁵³ A surfactant-coated species of sodium dodecyl sulfate was critical for achieving a reproducible nanotube dispersion and to obtain a homogeneous and stable solution.⁷ HNT is a polar inorganic filler full of ionic groups thus allowing it to blend directly with the polymeric carbohydrate without modification.

APPLICATIONS

Renewable carbohydrate polymers are hydrophilic and exhibit good dispersibility and biocompatibility, and CNT has extraordinary electrical, mechanical, and adsorption properties. Taking advantage of merits of both, the composites may have potential for applications in medicine and agriculture, and as biosensors, antistatic coatings, antistatic plastics, artificial muscles, corrosion protection, electronic paper, electronic shielding, environmentally sensitive membranes, and solar materials.^{5,22,54}

Sensors

Polymeric carbohydrate/CNT composites have great potential in sensing applications,⁵⁵ current progress in this field is mainly to set up a class of sensor materials with superior sensitivity, reduced size, and extended lifetimes for a wide range of environments and applications.¹³

Environmental Sensors. Conductive chitosan/CNT nanocomposite transducers processed using a spray LBL technique were highly sensitive toward not only polar vapours like water and methanol but also, to a lesser extent, to toluene.⁵⁶ Cellulose-MWCNT composite paper exhibited a sensitive, reversible and fast response to analytes with the following rank: methanol < ethanol < 1-propanol < 1-butanol. Interestingly, the composite paper could be used to identify n-propanol on the

grounds that the response to the concentration of 1-propanol was linear.¹³

Biosensors. Because carbohydrate polymers are biodegradable and compatible with biological organs, the application of carbohydrate polymer/nanotubes has been expanded to include biosensing. Cellulose/CNT composite was used to immobilize leukemia K562 cells on a gold electrode to form an impedance cell sensor. The sensor for leukemia K562 cells showed a linear range from 1.6×10^4 to 1.0×10^7 cells mL^{-1} with a detection limit of 2.6×10^3 cells mL^{-1} according to the 3σ rule.¹⁴ Nanobiocomposite chitosan film incorporating carboxylic group functionalized CNT was fabricated onto indium-tin-oxide (ITO) coated glass plate for coimmobilization of rabbit-immunoglobulin (*r*-IgGs) and bovine serum albumin (BSA) to detect ochratoxin-A (OTA). The results of electrochemical studies revealed that the presence of CNT resulted in increased electroactive surface area of chitosan leading to enhanced electron transport in these nanobiocomposites. Moreover, in chitosan/SWCNT and chitosan/MWCNT nanobiocomposites the availability of amine or hydroxy groups in chitosan and surface charged CNT also increased loading of the *r*-IgGs resulting in enhanced electron transport responsible for improved sensing characteristics.^{54,57}

Electroactive Paper (EAPap)

MWCNTs have been introduced to cellulose by mechanical blending as well as covalent grafting to overcome the drawbacks of cellulose EAPap. Carbon nanotube/cellulose composite materials were fabricated in a paper making process optimized for the formation of a CNT network on the cellulose fibers. The measured electric conductivity was from 0.05 to 671 S m^{-1} for 0.5–16.7 wt % CNT content, higher than that for other polymer composites.⁵⁸ Fugetsu et al. reported that CNT/cellulose paper containing 8.32 wt % CNTs was electrically conductive with a volume resistance of $5.3 \times 10^{-1} \Omega \text{ cm}^{-1}$.⁵⁹ MWCNTs covalently bonded to cellulose (cellulose esterification with MWCNTs) were used to fabricate reinforced EAPap.⁶⁰ The implementation of a homogeneous distribution of MWCNTs in a cellulose matrix with covalent grafting allowed for the reinforcement of mechanical properties and construction of stable electron pathways for paper transistors.⁶⁰ Glycerol plasticized-starch/MWCNT composites were also developed for potential electroactive isotropic electrical conductivity. The introduction of MWCNTs weakened the dependence of electrical conductivity on water content, and even eliminated it above the electrical percolation threshold of 3.8 wt % MWCNT loading. The electrical conductivity of the composite containing 4.75 wt % MWCNTs increased to $10^{\circ} \text{ S cm}^{-1}$, which was almost independent of the water content.⁴⁴

Electrodes

CNT/cellulose composite modified electrodes are promising for flow injection analysis, microchip capillary electrophoresis, enzymatic biofuel cells, and other microfluidic analysis systems.^{61,62} Glucose oxidase (GOx), a redox enzyme capable of oxidizing glucose as a renewable fuel using oxygen, was immobilized on a cellulose/CNT composite bioelectrode. GOx was encapsulated in this matrix and thereby immobilized on a glassy carbon surface. The direct electron transfer and electrocatalysis

of the encapsulated GOx was investigated using cyclic voltammetry and chronoamperometry. The GOx exhibited a pair of stable, well defined and nearly symmetric reversible redox peaks. The electrode with biocatalytic activity was sensitive toward the oxidation of glucose.⁶³ Chitosan scaffolds doped with MWCNT were impregnated into carbon to offer a robust macroporous electrode material that could be used in flow-through configurations as a microbial fuel cell (MFC) anodic material.⁶⁴ An alginate/CNT composite electrode was fabricated on the basis of *in situ* gelation of a mixture of CNTs and sodium alginate on the surface of a carbon disc electrode in aqueous calcium chloride solution. The electrode with CNTs embedded throughout the alginate matrix was reported to be used as a sensitive amperometric detector for capillary electrophoresis.⁶⁵ A MWCNT/ferrocene-branched chitosan composite-covered glassy carbon electrode was fabricated for the determination of sulfite.²⁷ A glassy carbon electrode (GCE) modified with carbon nanotube/chitosan (MWCNT-CHT/GCE) was used for the sensitive voltammetric determination of levodopa (Lev) and serotonin (Ser). The modified electrode was used for determination of Lev and Ser in human serum and urine with satisfactory results. The cyclic voltammograms displayed oxidation peak potentials corresponding to 50 mM of Lev and 35 mM of Ser compounds in phosphate buffer solution (pH 7.0) with a scan rate of 0.05 V s^{-1} at MWCNT-CHT/GCE. Lev, unlike Ser, showed a couple of redox peaks.³

Sorbents

Sorbents for Heavy Metal. Despite the high unit cost, chitosan/CNT beads could possibly be cost-effective sorbents for the removal of mercury from industrial waste in water treatment. The maximum Hg(II) removal values were 148.7, 183.2, 167.5, and 172.7 mg g^{-1} for chitosan, CMWCNT impregnated chitosan beads, MWCNT-impregnated chitosan beads, and SWCNT-impregnated chitosan composite beads, respectively.⁶⁶ A novel Schiff base-chitosan-grafted multiwalled carbon nanotube (S-CS/MWCNT) solid-phase extraction adsorbent was synthesized by covalently grafting a Schiff base-chitosan (S-CS) onto the surfaces of oxidized MWCNTs. The developed method was successfully applied to the determination of trace-metal ions in herring, spinach, river water, and tap water with good recoveries ranging from 91.0 to 105.0%. In short, the proposed method is suitable for preconcentration and separation of trace/ultra-trace metal ions in real samples.⁶⁷

Sorbents for Organic Pollutants. Iron oxide nanoparticles were synthesized at the surface of soluble starch grafted functionalized MWCNT to fabricate super paramagnetic nanocomposites with a saturation magnetization of 23.15 emu g^{-1} . MWCNT/starch/iron oxide composites exhibited better adsorption for anionic methyl orange (MO) and cationic methylene blue (MB) dyes than MWCNT-iron oxide. These magnetic MWCNTs possess the properties of adsorption capacity and magnetic separation and can therefore be used as magnetic adsorbents to remove organic contaminants from aqueous solutions.²⁴ An adsorbent made from calcium alginate/MWCNT composite fiber was prepared by wet spinning and used as an environmentally friendly adsorbent for the removal of MO from aqueous solution due to the efficient and fast adsorption process.³⁷

Fugetsu et al. have encapsulated MWCNTs in Ba²⁺-alginate matrix to constitute a cage and used it as the adsorbent for elimination of ionic dyes without the tedious centrifugation separation.⁶⁸

Biomedical Sorbents. Chitosan/MWCNT nanocomposite sorbents were used to successfully isolate hemoglobin from human blood. The coating of a layer of chitosan at the surface offers the promise of improved biocompatibility, hydrophilicity, and dispersion properties of CNTs without impairing the physical properties of MWCNTs or changing surface properties, thereby facilitating the biological/clinical applications of MWCNTs.⁶⁹

Biomaterials

In bone tissue engineering biomaterials containing polymers often are placed adjacent to bone. The use of CNTs in these biomaterials is anticipated mainly to improve their overall mechanical properties and they are expected to act as scaffolds to promote and guide bone tissue regeneration. There is a demand for utilization of biological macromolecules such as chitin, chitosan, gelatin, and recombinant proteins (bone morphogenetic proteins) along with CNTs which would direct and/or advance their application in bone tissue engineering.⁷⁰ Cellular studies of rat heart endothelial cells showed that SWCNT incorporated in alginate improved cell adhesion and proliferation.³⁵ Functionalized MWCNT-g-chitosan/hydroxyapatite scaffold, which has a micro-channel porous structure that extends through the whole monolithic dimension, was also developed as a biocompatible and biodegradable support for culture growth.²⁸

Electromagnetic Interference or Shielding Paper

Paper containing 8.32 wt % CNTs was electrically conductive with a volume resistance of $5.3 \times 10^{-1} \Omega \text{ cm}^{-1}$. The absorption efficiency increased as the frequency increased, reaching a maximum value of ~80% of the overall shielding efficiency at around 35 GHz. The overall shielding efficiency of the CNT/cellulose paper was found to be better than 20 dB in the entire frequency region (15–40 GHz) with a favorable value of about 40 dB at around 35 GHz. That is, highly flexible and tough composite paper composed of CNTs/cellulose fibers is capable of shielding electromagnetic interference over the tested range of 15–40 GHz, particularly in range of 30–40 GHz, with absorption as the essential shielding mechanism.^{59,71}

Textiles

Acid-treated SWNTs/cellulose (A-SWNT/cellulose) nanocomposites are a promising material that can be used for many applications, such as toughened Lyocell fibers, transparent electrodes, and so forth.¹² MWCNT/cellulose composite fibers were processed from solutions in ethyl methylimidazolium acetate (EMIAc). MWCNT containing solutions at 0.08 mass fraction of cellulose exhibited poor spinnability. To successfully spin the MWCNT/cellulose solution, the concentration of both cellulose and MWCNTs had to be lowered in the EMIAc. It was shown that EMIAc could effectively be used for solution spinning of cellulose/MWCNT composite fibers with enhanced tensile strength, reduced thermal shrinkage and good electrical conductivity. Such fibers could potentially be used in multifunctional materials such as electronic textiles or thermal barrier fabrics.¹⁵ A method was described for the wet spinning of alginate fibers

loaded with SWCNTs as high as 23 wt %.⁷² The nanotube-alginate fibers had unprecedented high flexibility and a very high electrical conductivity that was similar to semimetals (between germanium and carbon). MWCNTs were successfully incorporated in ultrafine cellulose acetate fibers by electrospinning,¹⁸ and the MWCNT/cellulose composite fibers had increased specific surface area, from $4.27 \text{ m}^2 \text{ g}^{-1}$, to 5.07 and $7.69 \text{ m}^2 \text{ g}^{-1}$ at 0.11 and 0.55 wt % MWCNTs, respectively, and much improved water wettability. The mechanical properties of the fibers were also greatly enhanced with increased MWCNT loading levels. The fact that MWCNTs were observed in only about a third of the fibers at a very low 0.55 wt % loading level suggests significantly higher tensile strength may be achieved by a further increase in MWCNT loading.¹⁸

At 0.05 mass fraction MWCNT, fiber tensile strength increased by about 25%, strain to failure increased by 100%, and modulus essentially remained unchanged. The composite fibers showed lower thermal shrinkage than the control cellulose fiber. The axial electrical conductivity at 0.1 mass fraction MWCNTs in these oriented fibers was more than 3000 S m^{-1} . At 140°C, the shrinkage in the control cellulose fiber was about 0.8%, 0.6% with 0.01 mass fraction of MWCNT, and 0.35% at 0.03 mass fraction of MWCNT. No further reduction in shrinkage occurred at higher MWCNT concentrations. The shrinkage reduction is consistent with good cellulose/MWCNT interaction.¹⁵

Packaging Film

Chitosan-treated MWCNTs dispersed well in the PVA matrix. Consequently the tensile properties and water resistance of the resultant nanocomposites were improved greatly compared with neat PVA. The improved properties suggest a great potential for the application of PVA/CS/MWCNTs nanocomposite films as a food packaging material to enhance the quality of packaged food.⁷³

CONCLUSIONS AND FUTURE PROSPECTS

The area of polymeric carbohydrate/nanotube composites has been progressing extremely rapidly and has achieved significant progress over last few years. A range of new composites have demonstrated astonishing mechanical parameters and conductivity values based on the fact that nanotubes themselves have remarkable electrical, thermal, and mechanical properties. Overall, the surface functions of NTs improve and expand their compatibility with carbohydrate matrices. Especially, covalently functionalized nanotubes have been shown to be particularly good additives for polymer reinforcement, allowing for an excellent stress-strain transfer between nanotubes and the polymer matrix. However, nanotube functionalization does not have any positive impact on the conductivity of cellulose/nanotube composites and normally results in higher percolation threshold values. Therefore, it is still quite challenging to achieve both good mechanical properties and high conductivity in one composite. To achieve the best performing nanocomposites the key issue is to balance the interfacial interactions between nanofiller and polymer matrix, the self-association of NTs and the organization of the carbohydrate matrices. In addition, mechanical dispersion, and/or post-processing techniques have great potential for the preparation of both mechanically strong and conductive

polymer composites. There is great interest in the further development of polymeric carbohydrate/nanotube composite materials, which are promising for a broad range of important applications. However, the current methods for preparation of NTs-based bionanocomposites are not suitable for practical manufacturing due to the lack of continuous processing technologies. Furthermore, environmentally friendly processing and manufacturing must be sought and/or developed in order to change the current status of the process from energy intensive, requiring strong/toxic chemicals and burdening our fragile ecosystem and environment. Future outlook includes development of such composites for use as alternative materials for various applications, including flexible electrodes in displays, bullet-proof vests, protective clothing, and high-performance composites for aircraft and automotive industries.

ACKNOWLEDGMENTS

The authors are grateful to National Natural Science Foundation of China (No. 21277073 & 51103073), Natural Science Foundation of Jiangsu Province (No. BK2011828), Scientific Research Foundation for the Returned Overseas Chinese Scholars, and Qing Lan Project and Six Talented Peak Program of Jiangsu Province and the Priority Academic Program Development of Jiangsu Higher Education Institutions for financial support.

REFERENCES

1. Shao, D.; Hu, J.; Wang, X.; Nagatsu, M. *Chem. Eng. J.* **2011**, *170*, 498.
2. Satarkar, N. S.; Johnson, D.; Marrs, B.; Andrews, R.; Poh, C.; Gharaibeh, B.; Saito, K.; Anderson, K. W.; Hilt, J. Z. *J. Appl. Polym. Sci.* **2010**, *117*, 1813.
3. Babaei, A.; Babazadeh, M. *Electroanalysis* **2011**, *23*, 1726.
4. Liu, M.; Zhang, Y.; Li, J.; Zhou, C. *Int. J. Biol. Macromol.* **2013**, *58*, 23.
5. Byrne, M. T.; Gun'ko, Y. K. *Adv. Mater.* **2010**, *22*, 1672.
6. Yun, S.; Kang, K. S.; Kim, J. *Polym. Int.* **2010**, *59*, 1071.
7. Suárez, B.; Simonet, B. M.; Cárdenas, S.; Valcárcel, M. *J. Chromatogr., A* **2006**, *1128*, 282.
8. Duarte, J. C. *FEMS Microbiol. Rev.* **1994**, *13*, 121.
9. Updegraff, D. M. *Anal. Biochem.* **1969**, *32*, 420.
10. Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 3358.
11. Lue, A.; Zhang, L. *Polymer* **2010**, *51*, 2748.
12. Kim, D.-H.; Park, S.-Y.; Kim, J.; Park, M. *J. Appl. Polym. Sci.* **2010**, *117*, 3588.
13. Yun, S.; Kim, J. *Sensor Actuat. B Chem.* **2010**, *150*, 308.
14. Wan, J.; Yan, X.; Ding, J.; Ren, R. *Sensor Actuat. B Chem.* **2010**, *146*, 221.
15. Rahatekar, S. S.; Rasheed, A.; Jain, R.; Zammarano, M.; Koziol, K. K.; Windle, A. H.; Gilman, J. W.; Kumar, S. *Polymer* **2009**, *50*, 4577.
16. Yan, Z.; Chen, S.; Wang, H.; Wang, B.; Jiang, J. *Carbohydr. Polym.* **2008**, *74*, 659.
17. Li, M.; Kim, I. H.; Jeong, Y. G. *J. Appl. Polym. Sci.* **2010**, *118*, 2475.
18. Lu, P.; Hsieh, Y.-L. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2413.
19. Ke, G. *Carbohydr. Polym.* **2010**, *79*, 775.
20. Brown, W. H.; Poon, T. *Introduction to Organic Chemistry*, 3rd ed.; Wiley: New York, **2004**.
21. Famá, L. M.; Pettarin, V.; Goyanes, S. N.; Bernal, C. R. *Carbohydr. Polym.* **2011**, *83*, 1226.
22. Yan, L.; Chang, P. R.; Zheng, P. *Carbohydr. Polym.* **2011**, *84*, 1378.
23. Swain, S. K.; Pradhan, A. K.; Sahu, H. S. *Carbohydr. Polym.* **2013**, *94*, 663.
24. Chang, P. R.; Zheng, P.; Liu, B.; Anderson, D. P.; Yu, J.; Ma, X. *J. Hazard. Mater.* **2011**, *186*, 2144.
25. Prusty, G.; Swain, S. K. *Polym. Compos.* **2013**, *34*, 330.
26. Rinaudo, M. *Prog. Polym. Sci.* **2006**, *31*, 603.
27. Zhou, H.; Yang, W.; Sun, C. *Talanta* **2008**, *77*, 366.
28. Honarkar, H.; Barikani, M. *Monatsh. Chem.* **2009**, *140*, 1403.
29. Liu, M.; Zhang, Y.; Wu, C.; Xiong, S.; Zhou, C. *Int. J. Biol. Macromol.* **2012**, *51*, 566.
30. Wu, T.; Pan, Y.; Bao, H.; Li, L. *Mater. Chem. Phys.* **2011**, *129*, 932.
31. Yang, C.; Liu, P. *Ind. Eng. Chem. Res.* **2012**, *51*, 13346.
32. Fabia, J.; Slusarczyk, C. Z.; Gawłowski, A. *Fibres Text. East. Eur.* **2005**, *13*, 114.
33. Liu, Y.; Chipot, C.; Shao, X.; Cai, W. *J. Phys. Chem. B* **2010**, *114*, 5783.
34. Liu, Y.; Chipot, C.; Shao, X.; Cai, W. *J. Phys. Chem. B* **2010**, *114*, 5783.
35. Yildirim, E. D.; Yin, X.; Nair, K.; Sun, W. *J. Biomed. Mater. Res. B Appl. Biomater.* **2008**, *87B*, 406.
36. Sui, K.; Li, Y.; Liu, R.; Zhang, Y.; Zhao, X.; Liang, H.; Xia, Y. *Carbohydr. Polym.* **2012**, *90*, 399.
37. Li, Y.; Sui, K.; Liu, R.; Zhao, X.; Zhang, Y.; Liang, H.; Xia, Y. *Energy Proc.* **2012**, *16*, 863.
38. Islam, M. S.; Ashaduzzaman, M.; Masum, S. M.; Yeum, J. H. *Dhaka Univ. J. Sci.* **2012**, *60*, 125.
39. Liu, L.; Wan, Y.; Xie, Y.; Zhai, R.; Zhang, B.; Liu, J. *Chem. Eng. J.* **2012**, *187*, 210.
40. Zhang, X.; Hui, Z.; Wan, D.; Huang, H.; Huang, J.; Yuan, H.; Yu, J. *Int. J. Biol. Macromol.* **2010**, *47*, 389.
41. Ma, L.; Wen, J. *Compos. Sci. Technol.* **2008**, *68*, 1297.
42. Qi, H.; Liu, J.; Gao, S.; Mäder, E. *J. Mater. Chem. A*, **2013**, *1*, 2161.
43. Cao, X.; Chen, Y.; Chang, P. R.; Huneault, M. A. *J. Appl. Polym. Sci.* **2007**, *106*, 1431.
44. Ma, X.; Yu, J.; Wang, N. *Compos. Sci. Technol.* **2008**, *68*, 268.
45. Liu, Z.; Zhao, L.; Chen, M.; Yu, J. *Carbohydr. Polym.* **2011**, *83*, 447.
46. Liu, Y.-L.; Chen, W.-H.; Chang, Y.-H. *Carbohydr. Polym.* **2009**, *76*, 232.

47. Wang, S.; Shen, L.; Zhang, W.; Tong, Y. *Biomacromolecules* **2005**, *6*, 3067.
48. Cao, X.; Dong, H.; Li, C. M.; Lucia L.A. *J. Appl. Polym. Sci.* **2009**, *113*, 466.
49. Zhang, H.; Wang, Z.; Zhang, Z.; Wu, J.; Zhang, J.; He, J. *Adv. Mater.* **2007**, *19*, 698.
50. Du, J.-H.; Bai, J.; Cheng, H.-M. *EXPRESS Polym. Lett.* **2007**, *1*, 253.
51. Kim, D. H.; Park, S. Y. *Fiber. Polym.* **2013**, *14*, 566.
52. Piri, N.; Mottaghitalab, V.; Arbab, S. *Fiber. Polym.* **2013**, *14*, 236.
53. Byrne, M. T.; Gun'ko, Y. K. *Adv. Mater.* **2010**, *22*, 1672.
54. Allen, B. L.; Kichambare, P. D.; Star, A. *Adv. Mater.* **2007**, *19*, 1439.
55. Kauffman, D. R.; Star, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 6550.
56. Kumar, B.; Feller, J. F.; Castro, M.; Lu, J. *Talanta* **2010**, *81*, 908.
57. Kaushik, A.; Solanki, P. R.; Pandey, M. K.; Kaneto, K.; Ahmad, S.; Malhotra, B. D. *Thin Solid Films* **2010**, *519*, 1160.
58. Imai, M.; Akiyama, K.; Tanaka, T.; Sano, E. *Compos. Sci. Technol.* **2010**, *70*, 1564.
59. Fugetsu, B.; Sano, E.; Sunada, M.; Sambongi, Y.; Shibuya, T.; Wang, X.; Hiraki, T. *Carbon* **2008**, *46*, 1256.
60. Yun, S.; Kim, J. *Sensor. Actuat. A Phys.* **2009**, *154*, 73.
61. Wei, B.; Guan, P.; Zhang, L.; Chen, G. *Carbon* **2010**, *48*, 1380.
62. Won, K.; Kim, Y.-H.; An, S.; Lee, H.-J.; Park, S.; Choi, Y.-K.; Kim, J. H.; Hwang, H. I.; Kim, H. J.; Kim, H.; Lee, S. H. *Appl. Biochem. Biotechnol.* **2013**, *171*, 1194.
63. Wu, X.; Zhao, F.; Varcoe, J. R.; Thumser, A. E.; Avignone-Rossa, C.; Slade, R. C. T. *Bioelectrochemistry* **2009**, *77*, 64.
64. Higgins, S. R.; Foerster, D.; Cheung, A.; Lau, C.; Bretschger, O.; Minteer, S. D.; Neelson, K.; Atanassov, P.; Cooney, M. J. *Enzyme Microb. Technol.* **2011**, *48*, 458.
65. Wei, B.; Wang, J.; Chen, Z.; Chen, G. *Chem. Eur. J.* **2008**, *14*, 9779.
66. Shawky, H. A.; El-Aassar, A. H. M.; Abo-Zeid, D. E. *J. Appl. Polym. Sci.* **2012**, *125*, E93.
67. Dai, B.; Cao, M.; Fang, G.; Liu, B.; Dong, X.; Pan, M.; Wang, S. *J. Hazard. Mater.* **2012**, *219*, 103.
68. Gong, J. L.; Wang, B.; Zeng, G. M.; Yang, C. P.; Niu, C. G.; Niu, Q. Y.; Zhou, W. J.; Liang, Y. *J. Hazard. Mater.* **2009**, *164*, 1517.
69. Chen, X.; Wang, W.; Song, Z.; Wang, J. *Anal. Methods* **2011**, *3*, 1769.
70. Sahithi, K.; Swetha, M.; Ramasamy, K.; Srinivasan, N.; Selvamurugan, N. *Int. J. Biol. Macromol.* **2010**, *46*, 281.
71. Zamora-Ledezma, C.; Añez, L.; Primera, J.; Silva, P.; Etienne-Calas, S.; Anglaret, E. *Carbon* **2008**, *46*, 1253.
72. Sa, V.; Kornev, K. G. *Carbon* **2011**, *49*, 1859.
73. Huang, D.; Wang, A. *RSC Adv.* **2013**, *3*, 1210.