We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

3,800 Open access books available
116,000 International authors and editors
120M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
1. Introduction

Carbon nanotube (CNT)-based transparent conductive film (TCF) technologies have potential applications in electrostatic dissipation (ESD), electromagnetic interference (EMI) shielding, and transparent film heating, as well as in the development of alternative electrode materials for touch panels and e-papers in display technologies, solar cells, flexible electronic devices, automobiles, and optical devices. In particular, single-walled carbon nanotube (SWCNT) network films have been intensively studied for the development of alternative transparent conductive electrodes due to their excellent electrical properties, the flexibility of SWCNT networks, and their solution processability under ambient conditions (Wu et al., 2004; Kaempgen et al., 2005; Zhou et al., 2006). For such applications, the optoelectronic properties of SWCNT-based TCFS should optimally be controlled by the material properties of the nanotubes, including purity, diameter, chirality, defects, metallicity, and doping level (Geng et al., 2007). Organic materials, such as conjugated polymers, block copolymers, polyelectrolytes, pyrenes, DNA, and so on, may also be used in applications because CNTs display good dispersion and stabilization in a variety of solvent media and polymer matrices. To maintain good electrical and mechanical properties, as well as environmental stability (e.g., thermal and hydrothermal stability), SWCNTs must be hybridized or top-coated with binder materials, such as cross-linkable polymers, ceramic sols, or metal oxide sols. The electrical properties of SWCNT/binder hybrid thin films are sensitive to their surroundings and to the interfacial structure of the network film, and the interfacial interactions or interfacial tension among nanotubes, binder materials, and substrates can affect the optoelectronic and environmental properties of SWCNT-based TCFS. (Han et al. 2009)

Despite these attractive features, fundamental studies and several advances are needed for the practical application of high-performance CNT films. This chapter describes some of the research conducted over the past 3 years that addresses these and other challenges, with an emphasis on our own efforts. We begin with critical properties of binders in CNT/binder hybrid thin films and then describe the various binder materials that yield high-performance CNT-based films via molecular or interfacial engineering at the interface between CNTs and binder materials. We conclude with some discussion of future directions and the remaining challenges in CNT/binder hybrid thin film technologies.
2. Carbon nanotube/binder hybrid thin films

To fabricate CNT/binder hybrid thin films by spraying or spin-coating, CNTs must first be well-dispersed in an organic solvent, and the dispersion stability should be maintained after mixing with the binder materials or additives. The wettability of the components in the CNT/binder mixture solution with respect to the target substrate should be considered. Here, interfacial engineering concepts may be applied to balance the interactions at the interfaces between the CNTs, solvent, additives, binder materials, and substrates (Fig. 1).

The conductivity, $\sigma_{DC}$, of a disordered nanotube film depends on the number density of the network junctions, $N_j$, which in turn scales with the network morphology though the film fill-factor, $V_f$, the mean diameter of the bundles, $<D>$, and the mean junction resistance, $<R_j>$, (Hecht et al., 2006; Lyons et al., 2008; Nirmalraj et al., 2009),

$$\sigma_{DC} = \frac{K}{<R_j>} \frac{V_f^2}{<D>^3}$$

Here, $K$ is the proportionality factor that scales with the bundle length. Note that changes in $<R_j>$ and $V_f$ via hybridization with binder materials may be influenced by the wetting properties of the SWCNT films.

The changes in CNT film sheet resistance after hybridization with binder materials may be understood in terms of the quantity of binder material and the interfacial tension of the
components (nanotubes and binder materials). The critical surface tension of a CNT sample falls within the interval 40–80 mN/m, and the cutoff value corresponding to \( \cos \theta = 0 \), \( \gamma_{\text{max}} \) falls within the interval 130–170 mN/m (Dujardin et al. 1994, 1998). Liquids with \( \gamma < \gamma_C \) yield complete wetting upon formation of a thin film. For \( \gamma_C < \gamma < \gamma_{\text{max}} \), partial wetting of the liquid occurs. The liquid does not wet a surface for \( \gamma > \gamma_{\text{max}} \). Most polymer materials with surface tensions of 30–50 mN/m wet CNT surfaces. Randomly oriented SWCNT network films include a large number of nanotube junctions. Such crossover sites attract polymeric materials via capillary effects (Dujardin et al. 1998). This means that the electrical properties of CNT/binder hybrid films can be controlled by modulating the interfacial tension between the CNT films and the binder materials or by modulating the quantity of binder material present. In addition, mixtures containing CNTs and a silane sol represent promising candidates for producing multifunctional coatings because the use of sol-gel chemistry to modify the properties of a gel with functionalized silane precursors has significant advantages. The sol-gel technique provides a method for fabricating ceramic materials and has been used to modify ceramic materials such as silica and TiO\(_2\) with CNTs. This section presents four methods for modulating the optoelectronic and environmental properties of CNT/binder hybrid films based on interfacial and molecular engineering. The first method uses the concept of a critical binder content to optimize the amount of binder material present with respect to the mechanical and electrical properties of the films. The second method uses molecular engineering to minimize or decrease the sheet resistance of the films or to fabricate multi-functional films by adding insulating binder materials or metal oxides. The last method uses a strategy to control the optoelectronic properties of films by matching the wettability of the coating solution on the substrates.

2.1 Critical binder content

The transmittance and sheet resistance of spray-coated CNT/binder films depend on the quantity of deposited CNTs and binder material, and on the ratio between CNT and binder. A plot of the sheet resistance as a function of binder content shows that above a critical binder content (\( X_c \)), the sheet resistance increases dramatically (Han et al., 2009).
strength of the interactions between the nanotubes and binder materials is also an important parameter that determines $X_c$, thereby influencing the junction structure. Figure 2 shows a plot of the transmittance vs. sheet resistance of the SWCNT/binder hybrid films with various binder contents. In this experiment, a methyltrimethoxy silane (MTMS) sol with a moderate surface tension was used as a model binder material. Here, the sheet resistance increased dramatically at a critical binder content. In this system, the critical binder content, $X_c$, was approximately 50 wt%. Above $X_c$, the CNTs were fully covered with the binder material, as illustrated in the scanning electron microscopy image (Fig. 2), which increased the contact resistance between the CNT network and the probe and decreased tunneling between CNTs through the insulating binder layer between the CNT bundles.

2.2 Molecular engineering for CNT/binder hybrid thin films

Increasing the interaction strength between a binder material and CNT surfaces is expected to increase the distance between nanotubes in a network film due to penetration of the binder material into network junctions. To investigate this interfacial interaction effect, model binder materials are required. A silane sol was used in this study to take advantage of the significant benefits associated with using sol-gel chemistry to modify the properties of a gel using functionalized silane precursors (Brinker & Scherer, 1990). The intermolecular interactions between the nanotube surfaces were controlled using a series of model binder materials: tetraethoxysilane (TEOS), methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS), and phenyltrimethoxysilane (PTMS), as shown in Fig. 3.

Fig. 3. A schematic diagram of the intermolecular interactions between SWCNTs and model binder materials: tetraethoxysilicate (TEOS), methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS), and phenyltrimethoxysilane (PTMS). (Han et al., 2009a)

The unpaired electrons of the silanol groups of the TEOS sol did not significantly polarize the negative charges on the nanotube surface and did not form favorable interactions. Hydrophobic interactions can arise between the methyl groups in the MTMS sol and the nanotube surface (Gavalas et al. 2001). The vinyl groups in VTMS and the phenyl groups in PTMS can interact with SWCNT surfaces via n-n interactions (LeMieux et al., 2008). The phenyl rings of PTMS may provide the best interfacial surface for CNTs due to strong n-n interactions. Moreover, the surface tension of the MTMS/VTMS/PTMS sol was less than 30 mN/m (Tillman et al., 1998), and that of the TEOS sol was around 170 mN/m (Ulatowska-jara et al., 2009). Therefore, the intertube or interbundle distances in the SWCNT/binder hybrid films could be modulated using these binder materials. This property was directly correlated with the electrical properties of the SWCNT/binder film because the sheet
resistance of the film resulted from the intrinsic resistance of the SWCNTs and the contact resistance at the junctions between nanotubes. The binder materials penetrated into the SWCNTs or the SWCNT bundles to increase the junction resistance. From this perspective, we expected the sheet resistance of the SWCNT/PTMS films to be the highest among all films tested because the PTMS increased the junction resistance in the network films.

As expected, the sheet resistances of the films gradually increased in the order of SWCNT/TEOS < SWCNT/MTMS < SWCNT/VTMS films. However, the sheet resistance of the SWCNT/PTMS film was lower than that of the SWCNT/MTMS film, even though the CNTs appeared to be well-distributed and covered with the binder material (Fig. 4d). Aromatic molecules, such as the phenyl-terminated silane used here, have been reported to interact and bind selectively to metallic SWCNTs because the polarizability of this silane is larger than that of the semiconducting nanotubes (LeMieux et al., 2008). Therefore, $R_s$ of the SWCNT/PTMS was lower than that of SWCNT/VTMS possibly due to interconnections between the nanotubes or nanotube bundles and the phenyl-functionalized silane sol via strong π-π interactions, which decreased the junction contact resistance. Raman spectral data provided evidence of bridging between the nanotubes and the PTMS sol. In a strongly aggregated state, for example a CNT network film without binder materials, van der Waals interactions between bundles dominated, whereas in a CNT/binder thin film, interactions between bundles and the functional groups of the binder materials influenced the Raman features. Binder materials with functional groups, such as nitro, amino, and chlorine groups, provided chemical doping effects via a charge transfer mechanism that influenced the conductivity of the nanotube films (Rao et al., 1997). However, in this system, doping effects
were excluded, and the G+ band was only slightly downshifted upon addition of the silane binder materials. This indicated that the functional groups acted as very weak electron-donating groups (CH₃, vinyl, phenyl) and the sheet resistances of the SWCNT/silane films were not significantly affected by charge transfer effects. Therefore, the dispersion state or the distance between nanotube bundles in the thin films appeared to dominate the conductivity in the CNT network films. The linewidth of the G+ band and the intensity ratio of the D and G bands were indicative of the degree of aggregation or bundling among the nanotubes. The enhanced resonance processes in the Raman scattering G band may have been due to exfoliation of the nanotubes, which decreased the D/G ratio of the G band. In addition, the relationship between the ratios I_D/I_RBM and I_D/I_G for laser excitation at 2.41 eV probed the aggregated state or the interbundle distances of bundles in the thin film network, assuming that the disorder defects were constant after hybridization (Liu et al., 2007). The high ratios of I_D/I_RBM and I_D/I_G indicated that the bundles were closely packed (Fig. 5d). The FWHM of the G+ band of the films exhibited a similar trend in the D/G ratio. The sheet resistances of the various silane binders followed a trend opposite that of the D/G ratio and the G+ band FWHM. These results, therefore, provide strong evidence that the average interbundle distance in the SWCNT/PTMS sol hybrid films did not differ from that in the pristine and SWCNT/TEOS sol hybrid films. The SWCNT bundles were presumably bridged by the strong interactions between the CNTs and the phenyl groups of PTMS, which contributed to the enhanced conductivity of the SWCNT networks, even though the CNTs were fully covered with insulating material, as determined by the top-view image. Such precise control over the optoelectronic properties of the SWCNT/binder films may be useful for fabricating high-performance conductive thin films, with ramifications for understanding the fundamental intermolecular interactions in carbon material science.

Fig. 5. (a) The correlations between the Raman spectral band at 1.96 eV (D/G ratio, FWHM of the G+ band) and the Rs (with an optical transmittance of 85%) for pristine SWCNTs and SWCNT/silane films. (b) Metallic components extracted from the G-band and G-band shift at 1.96 eV. (c) An illustration of the possible interactions between the SWCNTs and PTMS. (d) Correlation between the ratios I_D/I_RBM vs. I_D/I_G at 2.41 eV. (Han et al., 2009a)
2.3 Transparent, conductive, superhydrophobic CNT/binder hybrid films

If the wettability of conductive CNT films with high transmittance could be controlled via a superhydrophobicity (with a contact angle (CA) > 150°)-to-superhydrophilicity (CA < 5°) transition, this technology could potentially meet the needs of a wide range of applications that require multifunctional coatings (e.g., in optoelectronic devices, structural coatings, etc.). Many authors have focused on the fabrication and understanding of superhydrophobic surfaces, particularly those based on CNTs. However, most studies have not considered the optical properties of such CNT-based superhydrophobic surfaces. For applications in optical devices, transparency is one of the most important characteristics.

In nature, the leaves of many plants exhibit super water repellency (super-hydrophobicity) and are cleaned completely during a rain shower via the rolling of surface water droplets, which remove dirt and debris (self-cleaning) (Barthlott & Neinhuis, 1997). The unusual wetting characteristics of superhydrophobic surfaces are governed by both the chemical composition and the geometric microstructure of that surface. Wettability can be decreased or increased by creating a local structure that has a large geometric surface area in three dimensions relative to the projected two-dimensional area (Wenzel, 1936; Cassie & Baxter, 1944). Control over the wettability and optical properties may be achieved using mixed solutions containing CNTs and silane sols to produce multifunctional coatings. CNT networks control the nanostructure of the films, and silane compounds introduce a variety of chemical moieties on the top surface to provide particular mechanical properties.

Recently, we presented, for the first time, a facile method for creating transparent, conductive, superhydrophobic (or superhydrophilic) films from a one-component CNT/silane sol solution (Fig. 6). The stable CNT/silane sol solution relied on the intermolecular interactions between the hydroxyl groups of the H$_2$O$_2$-treated CNTs and the silanol groups of the silane sol. Moreover, the superhydrophobicity of the transparent (T > 90%) conductive films was enhanced by introducing nanoparticles into the coating solution.
The combination of the transparency and conductivity of CNTs with the chemical functionality of the silane binder would be beneficial to a wide range of CNT-based film applications, for example, development of self-cleaning optoelectronic coatings, transparent film heaters, electrostatic discharge coatings, and EMI shielding.

![Fig. 7. Water CA (triangles) and sheet resistance (R_s) (circles) versus transmittance of CNT/silane hybrid films (silane content = 70 wt%) without (red) or with (blue) silica nanoparticles. The upper image shows water droplets on transparent conductive films (the numbers shown in this image correspond to those in the plot). (Han et al., 2008)](image)

### 2.4 Hybridization with metal oxide

CNTs have been used to prepare a variety of hybrid materials that enhance the stability and functionality of CNT-based films by incorporating organic materials or inorganic oxides, such as SiO_2_, TiO_2_, SnO_2_, and ZnO. A successful strategy for fabricating the SWCNT/metal oxide films should employ a reliable means for forming stable solutions of SWCNTs and the metal oxide sol. The dispersion stability of SWCNTs functionalized with carboxylate groups (SWCNT-COOH) strongly depends on the ionic strength and pH of the solution. (Zhao et al. 2002) At pH < 3.0, SWCNTs are protonated, and they aggregate due to van der Waals forces and hydrogen bonding between protonated carboxylic acid groups. At pH > 3.0, mutual repulsion between tubes with charged carboxylic groups stabilizes the SWCNT dispersion. Organic or inorganic materials that contain amine groups can promote aggregation of the SWCNTs-COOH through hydrogen-bonded network formation. In particular, titania layers provide efficient shielding to prevent penetration of oxygen or moisture into the electronically active layer. (Lee et al. 2007) Uniform titania coatings on
CNT films constitute a potentially useful approach to enhancing the thermal and thermo-hydrostatic stabilities of CNT network films. Titania also acts as an electron transport material due to its high n-type carrier density and high electron mobility, which minimize junction resistance within the film network after hybridization to a binder material. Until now, titania coatings on CNT surfaces have been applied using highly functionalized multiwalled carbon nanotubes (Slazmann et al. 2007 & Gomathi et al. 2005) or benzyl alcohol (BA)-assisted noncovalent methods (Eder et al. 2008). However, functionalization by acid treatment decreases the conductivity of films. The BA method is not suitable for preparing TCF coating solutions because BA does not disperse SWCNTs in organic solvents and cannot stabilize titania sols during the coating process.

We recently reported that a complex formed between acetylacetone (acac, stabilizer of titania sol) and titanium in a titania precursor sol could be used to form a uniform titania layer on nanotube surfaces via hydrophobic interactions (Fig. 8). The thickness of the titania sol layer was controlled by varying the quantity of titania sol used in the solution. TEM images demonstrated formation of a uniform titania layer coating several nanometers thick on the surfaces of the SWCNTs. However, in the absence of acac, irregular titania formed because titanium atoms interacted selectively with carboxyl groups on the nanotube surfaces and amorphous carbon. The titania layer dramatically enhanced the thermal stability of the SWCNT films. The SWCNTs were easily oxidized at temperatures above 350°C, and the network in the SWCNT films was found to be disconnected (Fig. 9d). In contrast, the SWCNTs wrapped with a titania layer were stable under heating, as shown in Fig. 9c. Moreover, the titania layer provided positive effects on the electrical properties of the films via doping effects that operated under a charge transfer mechanism. Titania withdrew electrons from the nanotube surfaces, resulting in enhanced conductivity of the nanotubes. The D-band in the Raman spectra of functionalized SWCNT samples usually contains a broad peak upon which

Fig. 8. Mechanism for the noncovalent coating of SWCNTs with a titania layer, followed by removal of acetylacetone molecules by thermal treatment. (Han et al., 2010)
Fig. 9. SEM images of (a), (c) SWCNT/titania sol with acac and (b), (d) SWCNT/titania sol without acac containing 50 wt% titania sol; (a), (b) cured at 150°C, and (c), (d) baked at 350°C for 1 h. Right inset images in (a) and (b) show TEM images. Left bottom images in (b) show the chemical environment of the nanotube surface without acetylacetone. (Han et al., 2010)

is superimposed a sharper peak. The broad feature arises from amorphous carbon, and the sharper feature arises from carbon nanotubes. The narrowing of the D-band of titania-wrapped SWCNT (SWCNT@titania) films and the decrease of the carboxyl C1s peak in XPS after heating at 300°C indicated the removal of amorphous carbon without oxidation of the functionalized SWCNTs. The removal of amorphous carbon also decreased the sheet resistance of the SWCNT@titania films. Moreover, the ultrathin titania layer on the SWCNTs protected against water molecule absorption.

2.5 Wettability-controlled conductive films

Transparent conductive coatings based on CNTs are currently made using membrane filtration or spraying techniques. Spray application over a large irregular area is advantageous for high-throughput fabrication. Here, the wettability of the CNT/binder coating solutions on the substrates should be controlled during fabrication of highly transparent conductive thin films, because the film thickness is optimally smaller than several hundred nanometers. In this respect, the surface free energy of the substrate affects the surface properties and interfacial interactions, such as adsorption, wetting, and adhesion. Control over the wettability and optical properties may be achieved using a mixture of CNTs and silane sol, which is a promising candidate for producing multifunctional coatings. Sol-gel chemistry offers several advantages when used to modify the properties of a gel with functionalized silane precursors. Recently, we studied the
surface energy effects on the optoelectronic properties of CNT/binder hybrid films on glass substrates modified with silane layers containing various end functionalities. The CAs of silane-modified glasses were 67° for an NH2-functionalized surface, 96.5° for a CH3-functionalized surface, and 112° for a CF3-functionalized surface (Fig. 10).

The sheet resistances gradually decreased with increasing wettability of the coating solution on the substrates. Although the transmittance of the films changed very weakly (T changed from 92.3% to 91.2% in moving from a CF3-functionalized to an OH-functionalized surface), the sheet resistance of the film on the OH surface was an order of magnitude smaller than the counterparts prepared on a CF3-functionalized surface, giving a very low surface energy. This result is significant because the sheet resistance can change dramatically for high transmittance films. SEM images of the CNT/MTMS sol hybrid films clearly showed that the hydrophilic surfaces were more homogeneous than the hydrophobic surfaces. A decreased surface energy increased the heterogeneity of the surface morphology. In particular, the most hydrophobic surfaces (containing CF3 groups) clearly showed a dewetted pattern after spray-coating, which may explain the slightly higher transmittance of the film. Nevertheless, the sheet resistance of this film was sufficient for transparent ESD films. The CNTs were macroscopically connected with a fractal dimension of 1.77 for the film surface. The dark regions in the SEM images indicate the low-CNT-density areas (mostly binder materials), as shown in Fig. 11. The low sheet resistance and high transmittance of the film prepared on a CF3-functionalized surface was explained in terms of the submicrometer-scale disconnect between CNTs, as shown in Fig. 15d. These results indicated that the sheet resistances of highly transparent CNT/binder hybrid films were easily modulated by controlling the wettability of the CNT/binder mixture solutions on the substrate. Previous studies by Kim et al. also attempted to improve the transparency of CNT films by adjusting the CNT network density using a two-dimensional colloidal crystal template. (Kim et al. 2008)

Fig. 10. Schematic representation of the spray coating of FWCNT/silane solutions on surface-modified model substrates. (Han et al., 2009b)

These results have important implications for the fabrication of highly transparent conductive films from CNTs and binder solutions. Although we used a polar solvent and a hydrophilic binder material in this study, our method is applicable to a variety of coating solutions prepared using other solvents and binder materials on various substrates, such as...
poly(ethylene terephthalate), polyether sulfone, and polycarbonate. Moreover, we suggest that the transparency of CNT/binder films can be improved by manipulating the CNT density in the film, which can be achieved by adjusting the wettability of the coating solution or by forming dewetted areas with different surface energies, because the conductivity and transparency of a film depend primarily on the CNT density.

Fig. 11. Scanning electron microscopy images of CNT/MTMS thin films on various substrates; the surface functionalities are: (a) OH, (b) NH₂, (c) CH₃, and (d) CF₃. (Han et al., 2009b)

3. Summary

Research into CNT/binder hybrid thin films over the last few years has yielded significant progress in controlling the optoelectronic properties of the films by modulating the balance of interactions at the interfaces among the components: CNTs, solvent, additives, binder materials, and substrates. A critical binder content was identified, above which the sheet resistance increased dramatically, and this value was found to depend on the interfacial tension between the CNTs and binder materials. At the same time, effective methods were developed for minimizing or decreasing the sheet resistance by adding insulating binder materials. The transparent, conductive, superhydrophobic coating technology relies upon controlling the surface nanostructure and chemical state of the surface. The thermal and environmental stability of the SWCNT films were enhanced by noncovalent wrapping by a titania layer. The optoelectronic properties of the CNT/binder hybrid films were modulated by controlling the wettability of the coating solutions on the substrate.

Significant challenges to this technology remain. First, strategies for minimizing the junction resistance in a random network structure must be developed for applications such as high-performance CNT-based TCFs. Second, improved hybridization methods using various
ceramic oxides or metal oxides are needed to use these films in multifunctional electronic devices, such as sensors, actuators, and thin film heaters.

4. References


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

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:
