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Strategies to Successfully Cross-Link Carbon Nanotubes

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1. Introduction

Since the inception of the research field on carbon nanotubes (CNTs), there has been an enormous effort to understand how the tubes form and how to best garner their unique electronic and mechanical properties. It soon became apparent that in order to develop the next generation of functional materials, a way to modify the surface of the tubes and connect them was required. The development of the oxidation process with acids was the first revolution in the field of CNTs, potentially opening the door to an extensive library of modifications. Research progressed by integrating the nanotubes into composites at low concentrations with some success, but the goal of producing high nanotube component covalently cross-linked materials was still problematic. Two decades after the report by Sumio Ijima on their discovery, cross-linked CNT materials are still difficult to produce, and this has shifted the field towards a back-to-basics approach to try and solve the problem. One key problem identified was the presence of lattice fragments immobilized on the surface of the CNTs (Fig. 1.). The current methods of characterization such as X-ray photoelectron, Infrared and Raman spectroscopy are indirect and generally fail to distinguish between the surface attached functional groups and oxidized lattice fragments. A CNT washing technique has been developed to remove these fragments and any electrostatically attached products to allow pure covalent interactions with the surface of the nanotube (Wang *et al.*, 2010). With an industry now thriving on the production of cheap functionalized carbon vapor deposition (CVD) CNTs, priced according to the percentage surface functionalization, and the decline in published materials on arc-produced CNTs, the need for effective characterization and quality control increases.

It is the intention of this chapter to review some of the successful approaches used to cross-link CNTs with a focus on the importance of the chemistry and techniques involved, and highlight two areas of research we are currently investigating at Florida State University.

1.1 The characterization dilemma

As the basic unit for nanotubes, single-walled carbon nanotubes (SWCNT) have been envisaged as a solution in areas such as molecular wires to biological transport vectors, however in order to reach this potential, we need to be able to modify the surface structure. The solubility of SWCNTs is on average 0.1 mg/ml, however this can be increased to 1 mg/ml with surface modification. The problem with this form of modification is that the inherent properties of the nanotubes, both the mechanical and electronic properties, can be significantly altered, questioning the reasons for modifying the tubes.

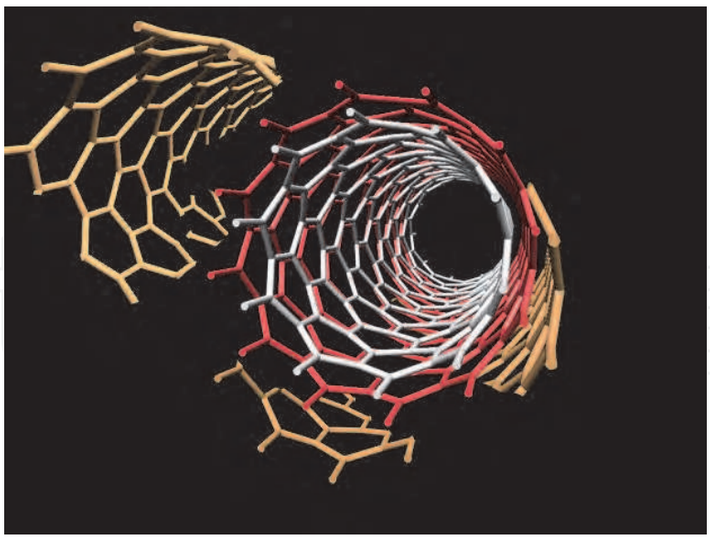

Fig. 1. A carbon nanotube with lattice fragments on the surface. These fragments can be easily oxidized and result in an incorrect assessment of the degree of CNT surface functionalization.

One aspect of CNT research that can prove discouraging at times is the difficulty in the direct characterization of functional moieties after a chemical process. Sidewall functionalization is important for the use of the tubes in cross-linked composites. One of the most popular techniques used in journals was Fourier Transform Infrared Spectroscopy (FTIR). Whilst it is a powerful technique in organic chemistry, for CNTs it is difficult to prove the presence of covalently attached groups although there are good indications of hydroxyls, carbonyls and amine derivatives. The low concentration of functional groups on the surface is also a problem for acquiring a sufficient signal and the generation of a good baseline requires careful preparation. Raman spectroscopy is extremely popular due to the characteristic D-band that measures the degree of disorder and the G-band that provides a measure of the sp^2 character. While the ratio of the bands can provide an insight into the quality of the tubes, it can be difficult to form a correlation between the distribution of the functional groups and the ratio of the bands. UV spectroscopy (UV) requires the nanotubes to be dispersed at a low concentration which is difficult, as the CNTs tend to sediment during acquisition. Visual techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM) can be useful for identifying regions and trends, but the sample area is small for TEM and there are charging issues with SEM. Table 1 gives an overview of the types of issues encountered with characterization.

2. Cross-linking methods

In this section, we will discuss some of the successful methods employed to facilitate the cross-linking of CNTs. There are a variety of methods available and theoretical studies have shown the possibility of the assembly of higher ordered structures, however the examples listed here differ in the approach to cross-linking from aspects of defunctionalization to nanocrystal interactions.

Methods	Type	Information	Limitations of Technique
TGA	Solid	Functionalization ratio	No information on covalent modification.
XPS	Solid	Elements present and the functionalization ratio	Inference of covalent attachment but quantification is restricted
Raman	Solid	Degree of disorder and sp^2 character	No direct chemical information and interpretation is problematic
Infra red (IR)	Solid & Liquid	Groups	Analytical quantification not advisable
UV/visible	Liquid	Sidewall functionalization	Solubility of sample is difficult
AFM	Solid	Topography	Sample size is small. No information on the covalent functionalization and no chemical identity
TEM	Solid	Transmission Image, Lattice	Sample size is small. Inference of covalent functionalization only.
SEM	Solid	Secondary electrons	No chemical identity

Table 1. A list of the limitations of the characterization techniques typically applied to CNTs. Table adapted from a module by Liling Zeng and Andrew R. Barron.

2.1 Cyclo-addition reactions

The side-wall functionalization of CNTs is of great importance, primarily for increasing the solubility of tubes, but equally important is the ability to process the CNTs to form composites. One successful method is that of nitrene chemistry. Nitrenes (R-N:) are structurally similar to carbenes (RR'C:) and are electron-deficient uncharged molecules, which depending on the side groups, can facilitate addition and rearrangement reactions. The singlet nitrenes can react with the sidewall of CNT's by electrophilic [2+1] cyclo-additions or by inter-system crossing. The triplet state reacts with the π system of the CNT with both the singlet and triplet states resulting in the formation of aziridine rings (Fig. 2A).

Cross-linking was achieved by using a di-azidocarbonate, based on poly-ethylene glycol (PEG) (Holzinger *et al.*, 2004). The preparation of the cross-linked nanotubes is a simple process using SWCNTs dispersed in 1,1,2,2-tetrachloromethane (TCE) by sonication. The suspension is then heated to 160 °C and a 20-fold excess of diluted di-azidocarbonate in TCE is added over a period of 30 mins. After cooling, the mixture is filtered and washed with TCE and ethanol. This process is highly effective in cross-linking, but because of the length and flexibility of the cross-linker it is possible for the linker to attach to the same tube forming a loop (Fig. 2B).

The characterization of the composite was performed by using a range of techniques including transmission electron microscopy, atomic force microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. This cyclo-addition technique holds huge promise for the development of further films using long chain nitrene based cross-linkers.

2.2 Ion beam and irradiation techniques

One other method of cross-linking carbon nanotubes is through electron or ion beam irradiation. It has been theorized that cross-linking nanotubes could improve the overall characteristics of nanotubes on the bulk scale. While this method can be achieved on both SWCNTs and MWCNTs, this technique of cross-linking has both its advantages and disadvantages. One advantage is that the setup is simple and there are no chemical reactions that need to be performed. Another advantage is that the bonds formed between the tubes are much stronger than the van der Waals interactions that are sometimes used to link nanotubes. In addition to this, not only can individual tubes be cross-bonded, but it has been demonstrated that it should be possible to link macroscopic carbon structures such as CNT mats and fibers. According to simulations, ion irradiation will affect SWCNTs and MWCNTs differently. The incident energy from irradiation will scatter carbon fragments from a SWCNT, and a percentage of these fragments will be redistributed along the nanotube surface. In the end, these fragments will form the cross-links between the nanotubes. It was predicted that a much higher percentage (~50%) of the fragments will be redistributed between the inner walls of MWCNTs. Therefore, cross-linking via irradiation is more suitable for SWCNTs but it can still be used to reinforce the inner walls of a MWCNTs. These theoretical predictions for cross-linking nanotubes have been confirmed experimentally by researchers. An improvement in electron transport properties in bundles of SWCNTs due to increased intertube coupling, after exposure to an Ar^+ beam, has also been demonstrated (Stahl *et al.*, 2000). It has been shown that electron irradiation of MWCNTs can reinforce the inner walls (Fig. 3.) and stiffen the tubes by up to five times (Duchamp *et al.*, 2010). Studies have also looked into the possible mechanisms involved in the radiation induced modification of CNTs (Kis *et al.*, 2004). Similar results have been reported (Peng *et al.*, 2008) and have demonstrated improvements in fracture strength.

Despite all these advantages and promising results for irradiation cross-linking, there are a few drawbacks. One disadvantage is that it destroys the sp^2 bonding of the nanotube which could be detrimental to the tubes' intrinsic properties. Another disadvantage of this technique is that the cross-linking capabilities are dependent on where the nanotube can be exposed to the electron or ion beam. If you wanted to produce a cross-linked nanotube mat (similar to buckypaper) only the surface layers of the CNT mat would be cross-linked as the interior tubes would not be exposed to the incident beam.

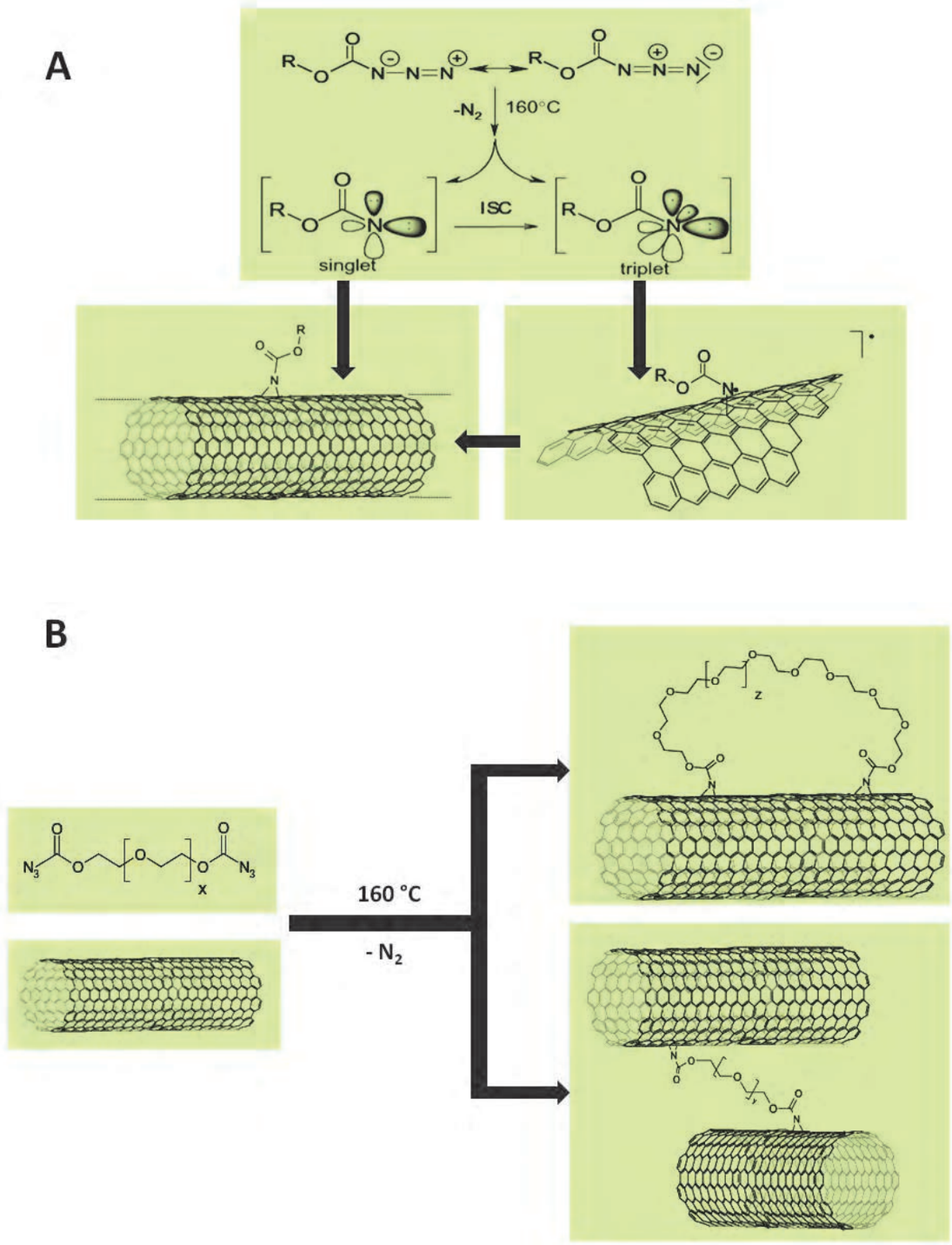

Fig. 2. A) Schematic presentation of the reaction of nitrenes with the nanotube sidewall. B) Reaction of di-nitrenes with the nanotubes using diazidocarbonate polyglycolesters as precursors. The addition of the di-functional molecule can also happen on the sidewall of the same CNT resulting in the formation of a loop. Adapted from (Holzinger *et al.*, 2004)

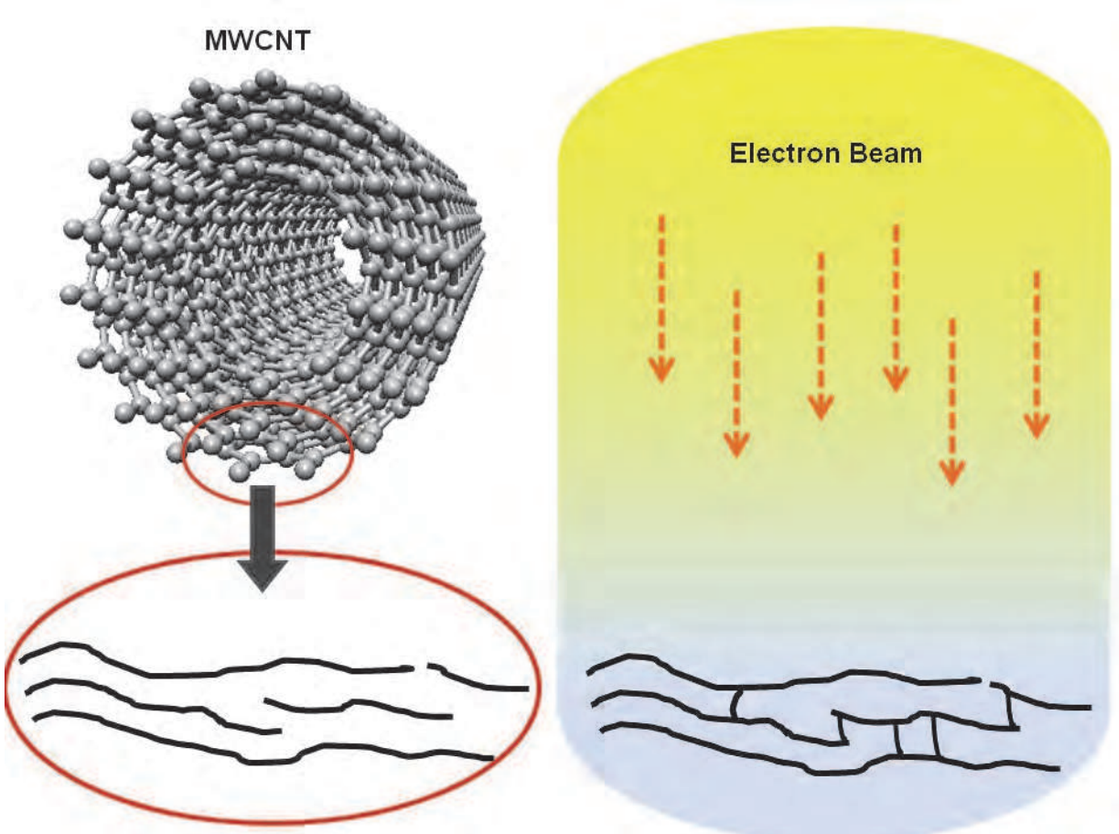

Fig. 3. The reinforcement of the sidewalls of a MWCNT by an electron beam. This form of cross-linking may be extended to neighboring tubes forming a covalently linked intertube junction.

2.3 Michael addition

At Florida State University we have been exploring the nature of cross-linking between CNTs. Inspired by the interaction of maleimides with cysteine for biological labeling and the potential for the covalent interaction of CNTs, we used benzoquinone to cross-link thiolated carbon nanotubes (MWCNT-SH) to form mats similar to buckypaper. We wanted to develop a way of producing a cross-linked mat without the need to use high pressure processes or electron beams to fuse the tubes together, so we applied a back-to-basics approach and tried to identify the problems associated with poor cross-linking between the tubes. It became apparent that the inability to control reaction conditions during the formation of the mats was a problem so we attempted to maintain the temperature and dispersion of the tubes until the mat was ready to be cast. The procedure involved sonicating MWCNT-SH (1g, Nanocyl) with an excess of dithiothreitol (DTT) to separate the nanotubes and break up the disulfide bonds. The MWCNT-SH were then washed with DMF and dried for 12 h. From this batch, MWCNT-SH (20 mg) were dispersed in DMF (15 ml) and sonicated. In a separate vial, benzoquinone (100 mg) was dissolved in DMF (10 ml). The benzoquinone solution was slowly added to the nanotube suspension and the mixture was stirred at 75 °C for 12 hours before being vacuum filtered and washed with excess DMF. It

was noted that the use of a heat gun to maintain the temperature of the mixture at 75 °C aided cross-linking during filtration (Ventura *et al.*, 2010).

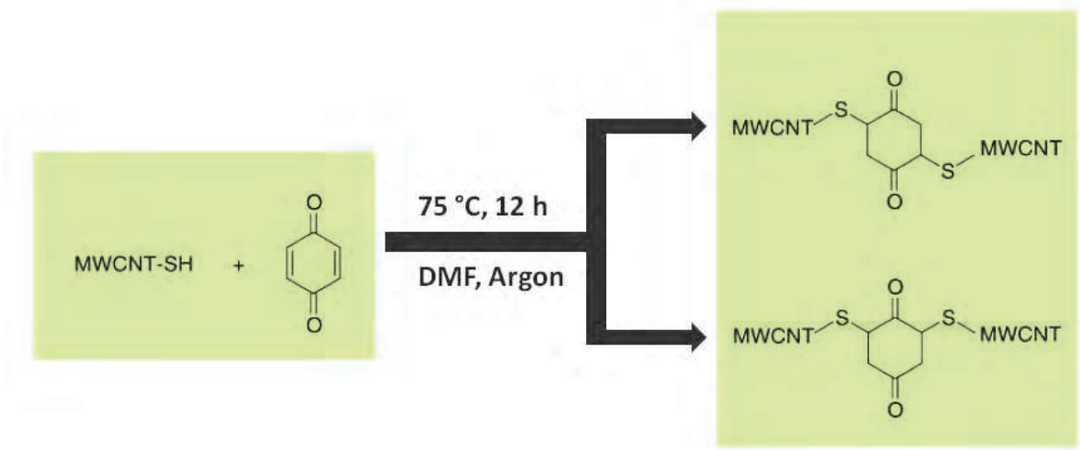

Fig. 4. Reaction scheme for cross-linking MWCNT-SH with benzoquinone.

The products formed during the reaction are of two forms, either the 2,5-dithioMWCNT 1,4-cyclohexanedione adduct or the 2,6-dithioMWCNT 1,4-cyclohexanedione adduct depending on the steric interactions (Fig. 4.). Several concentration ratios of benzoquinone : MWCNT-SH were tested to obtain the optimum flexibility of the mat produced. Tensile strength measurements indicated that the optimum concentration of benzoquinone : MWCNT-SH was 5:1 and the SEM images inferred the that there was sufficient cross-linking (Fig. 5A) The 10:1 composite produced a brittle mat confirming the link between the increasing strength of the mat and the degree of cross-linking.

The surface of the 5:1 nanotube film also contained unreacted thiol groups that were used to attach nanocrystals to enhance the functionality. As a demonstration of this principle, we attached 5.7 ± 0.3 nm gold particles to the surface (Fig 5B).

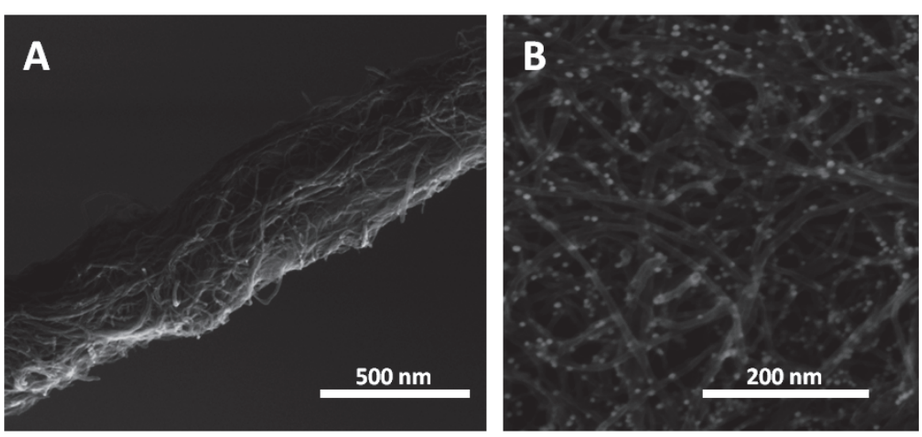

Fig. 5. A) The SEM images of a cross-linked bundle of nanotubes and B) a nanotube mat decorated with 5.7 ± 0.3 nm gold particles.

Once the film was produced we wanted to see if we could create a die-cast composite using a 10:1 ratio of benzoquinone : MWCNT-SH. During this procedure, we injected a predrilled cast, in the letters "FSU", with the cross-linking mixture of benzoquinone and MWCNT-SH and placed the cast on a hotplate heated to 75 °C. We periodically injected more of the mixture as the liquid level dropped until the cast was full, and left the cast at 75 °C for 9 hours before cooling to room temperature (Fig. 6A). The cross-linked FSU blocks were removed with the aid of a scalpel in smaller blocks (Fig. 6B).

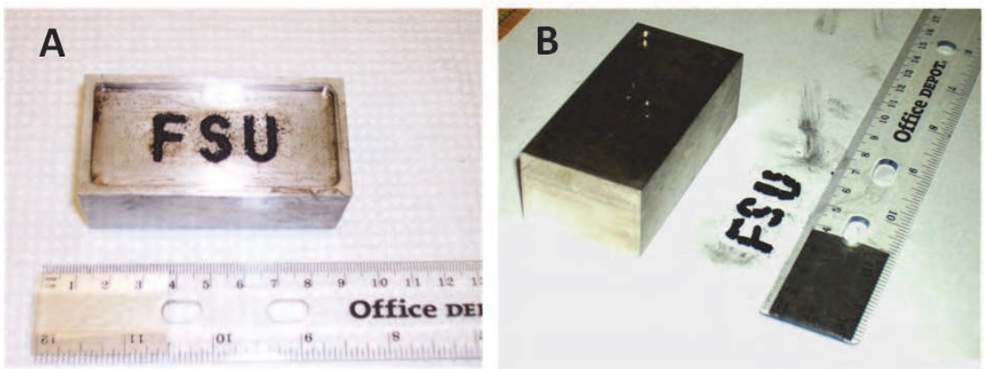

Fig. 6. A photograph of A) the letters FSU cast into a stainless steel container with a 10:1 mixture of benzoquinone : MWCNT-SH injected into the cast. B) The cross-linked composite removed from the cast after heating.

Although the removal of the composite from the cast was difficult, it was primarily due to the design of the cast. We plan to explore the use of bismaleimide groups to generate similar composites. We are also exploring alternative methods to modify the carbon nanotubes. One method that we find intriguing is the use of a mechano-chemical approach. This is a novel method in the field of CNTs and provides an alternative route to attach functional groups to the surface of CNTs by ball-milling the tubes in the presence of a reactive gas. The milling creates defects on the tubes which react with the gas forming covalent attachments (Konya *et al.*, 2002).

For cross-linking, it is preferential to have a fairly uniform CNT size and distribution of functional groups on the surface. Both of these requirements were addressed in research into the mechano-chemical functionalization of CNTs with a ball mill, for the generation of surface thiols, chlorides, acyl chlorides, amines and amides.

The process involved placing purified CNTs into a ball-mill and degassing in a heated N_2 environment or in a vacuum. The reactant gas was then pumped through the chamber untill the milling process was complete. The excess reactant is removed by the evacuation of the chamber, and the tubes are subsequently washed with ethanol. The research noted that extended periods of milling resulted in the generation of amorphous carbon and lattice fragments with a 30-35% amorphous content formed after a period of 2 weeks. The milling process shortened the tubes and this was also carefully controlled by the cumulative milling time.

The results inferred that the CNTs obtained had a high degree functional groups around the surface as indicated by IR and XPS, and the process can be scaled up depending on the size of the mill.

2.4 MWCNT-Titania films

There are many theoretical ways to improve the photocatalytic efficiency of titania (TiO_2) including increasing the surface area of TiO_2 or creating methods to promote charge separation, but there needs to be a better way of promoting electron transport. Therefore, the development of new materials that are capable of increasing the efficiency of electron mobility are required. CNTs are known to be a good candidate for use with TiO_2 because of the semiconducting and metallic behavior depending on the diameter of the tubes and helicity. Enhancing the photocatalytic properties of titania is extremely important, especially when it is considered as a potential for the photocatalytic reduction of CO_2 with H_2O (Xia *et al.*, 2007). Titania itself exhibits good photostability properties; however the photocatalytic reaction with CO_2 is insufficient for applications. This problem was reduced significantly by the application of carbon nanotubes as a mediator of electron transfer and MWCNTs have been investigated for their charge transfer properties with titania, but a suitable composite needs to be constructed.

We have constructed a nanotube film which uses aminated titania particles as a cross-linker for CNT films (Fig. 7.). In a departure from the standard cross-linking theory, we wanted to examine the potential for these beads to act as cross-linkers in CNT films. In addition to the formation of amide bonds, the nature of interaction allows for the potential of electron transfer from TiO_2 to the carbon nanotubes.

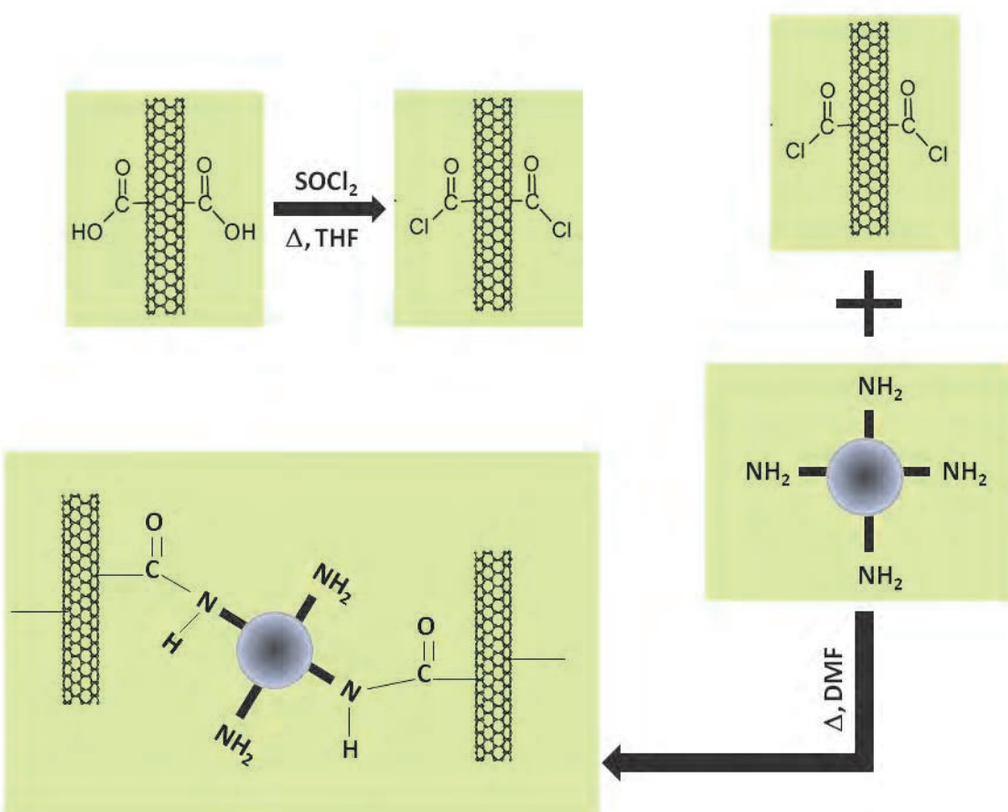

Fig. 7. Reaction scheme of the acylation of CNTs followed by the cross-linking of an aminated titania bead.

MWCNT-COOH (1 g, 50-80 nm OD, Nanostructured & Amorphous Materials Inc.) were converted to MWCNT-COCl by heating the nanotubes under reflux for 3 days in THF with thionyl chloride. The MWCNT-COCl were washed with excess THF under vacuum and the tubes were dried over a period of 24 h. The MWCNT-COCl (100 mg) were sonicated for 10 minutes whilst TiO_2-NH_2 (25 mg/ml, Corpuscular Inc.) 100 nm particles (Fig. 8A) were added. The mixture was further heated under reflux and slowly vacuum filtered whilst hot to produce a thick film. The films were brittle but the SEM images indicated a sufficient dispersion throughout the composite. The particles are amorphous but can be easily converted to anatase or rutile by heating, making the film a good candidate for photocatalytic activity.

Using particles and nanocrystals as cross-linking agents is of great interest for increasing the surface area for reactivity. Examples can found in literature of the use of such constructs in the formation of photoreactive composites of CNTs and titania (Yao *et al.*, 2008) and Pt nanoclusters/titanium dioxide nanotube composites (Dong *et al.*, 2010). In order to increase the utility of these composites, they would need to be processed into films to fully take advantage of their unique properties.

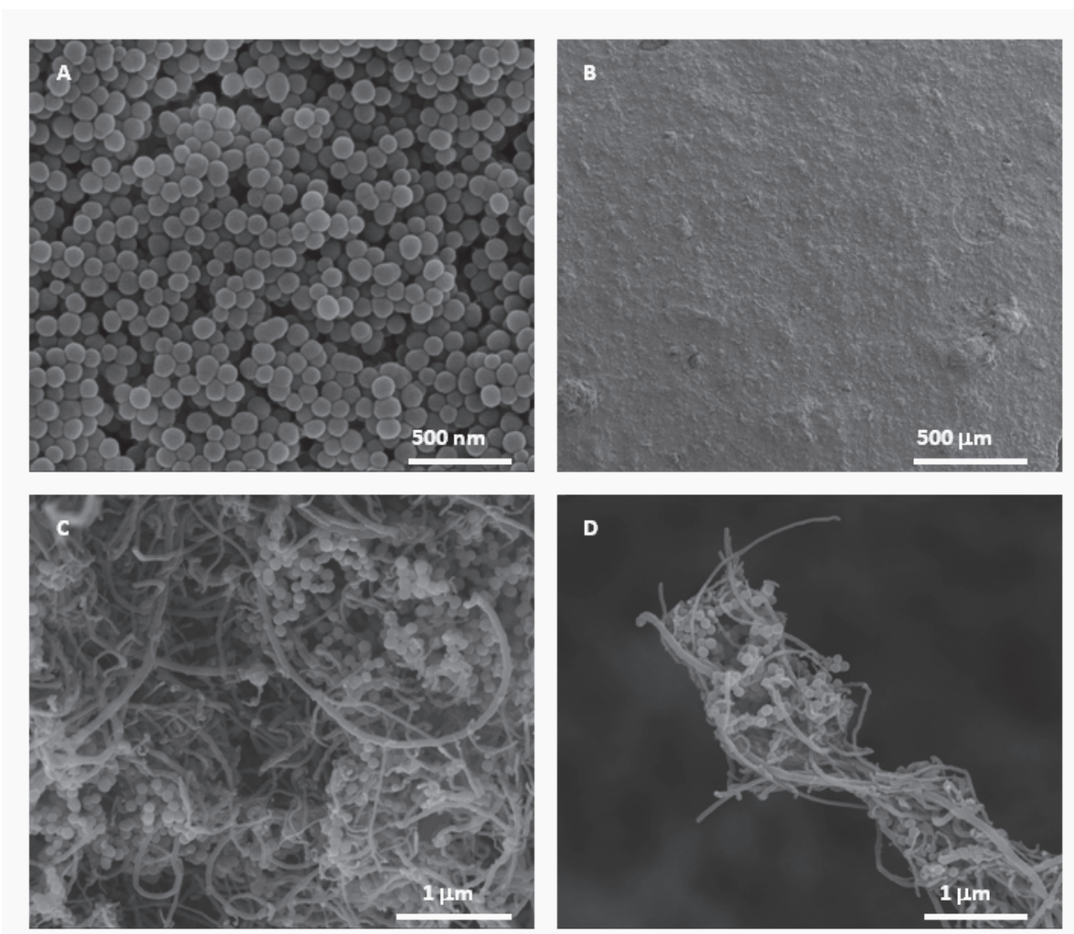

Fig. 8. SEM images of A) aminated titania particles B) low magnification image of the film C) a high magnification section of the film surface D) A highly cross-linked fiber at the edge of the film.

2.5 De-fluorination

The ultimate goal of cross-linking carbon nanotubes is to find a way of incorporating the effectiveness of the electron beam techniques with a chemical approach. This concept was highlighted by the work demonstrating the production of binder free cross-linked carbon nanotube composites (Sato *et al.*, 2008). The problem addressed in their research focused on an additional issue with CNT chemistry. CNTs with smaller diameters are typically more reactive than larger MWCNTs because the strain energy is inversely proportional to the diameter of a tube. The surface of larger MWCNTs act like a graphite sheet making surface modifications extremely difficult. One solution to this was the fluorination of CNTs, and this was achieved by reacting purified MWCNTs with a mixture of 20% F_2 and 80% N_2 at 523 K for a period of 2 hours followed by thermal annealing at 523 K for 6 hours under N_2 (Sato *et al.*, 2008). The cross-linking of the CNTs was achieved by using a spark plasma sintering system that produces a significant amount of sp^3 carbons, which connect the tubes when operated for 10 minutes below 80 MPa. Fig. 9A shows a picture of the defunctionalized block. The size and dimensions can be tailored depending on the vessel used to cast the block.

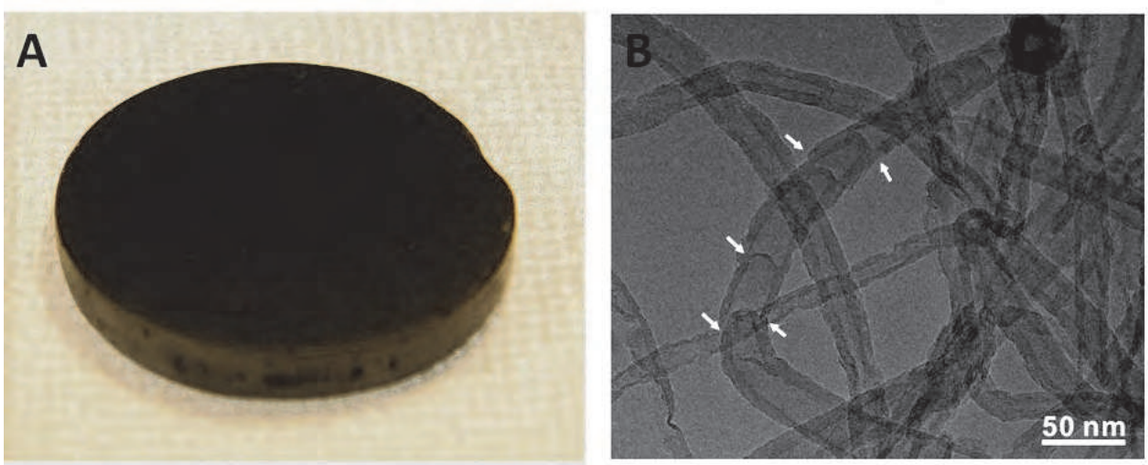

Fig. 9. A) The photograph of a defunctionalized MWCNT block and B) a TEM image of a cross-linked composite showing bamboo-like structures, at the white arrow positions. Adapted from (Sato *et al.*, 2008)

Fig. 9B shows a characteristic high magnification image of the block. The bamboo-like structures have been seen in nitrogen doped carbon nanotubes, however in this case they are the result of the CVD process and beneficial for exploiting defect sites.

The spark plasma sintering solidification process also more accurately relies on the liberation of carbon fluorine gases which generate defects and vacancies on the MWCNT surface, effectively increasing the reactivity. The comparison of the block with commercially available graphite (Table 2.) shows a greater percentage porosity which may indicate a future avenue to tailoring the material for applications such as hydrogen storage. The Vickers Hardness has a value of 46.9 MPa which is much higher than that of graphite at 16.8 MPa, but lower than the minimum value for carbon steel calculated to be approximately 539.4 MPa. It is surprising that the conductivity is slightly more than that of graphite given the increase in sp^3 character, but this may be a result of the bulk properties of the composite rather than the dominance of individual tubes. The process is still highly destructive for the

outer layer of MWCNTs and detrimental to that of SWCNTs, which means the fluorination process would have to be carefully controlled to prevent extensive damage. Future work on this type of cross-linking may require the relationship between the fluorination time and de-fluorinated cross-linking ability to be established.

Characteristic	De-F-MWCNT Blocks	Commercial Graphite
Bulk Density, ρ(g/cm^3)	1.44	1.74
Porosity (%)	36.2	23.0
Young's Modulus, E_b *(GPa)*	14.2–16.3	6.5–8.6
Fracture Bending Strength, σ_b (MPa)	92.4–123.0	42.1–43.7
Vickers Hardness, H_v*(MPa)*	46.9	16.8
Conductivity, σ (S/cm) (four-probe)	2.1 X 10^2	6.0 X 10^2

Table 2. The properties of the de-fluorinated MWCNT blocks in comparison to commercially available graphite. Adapted from (Sato *et al.*, 2008).

In general, the cross-linking by de-fluorination is possibly one of the best methods for producing strong-robust carbon materials. If the process can be further refined, it may also be possible to create thin films for filtration or flexible films for catalytic substrates.

3. Applications of cross-linked CNTs

CNTs have been linked to diverse fields from biomedical drug delivery vectors to nanoscale computing. This section highlights some of the applications envisaged for the tubes, focusing on the development of non-covalent and covalently intertwined architectures, and the importance of the techniques used for their assembly.

3.1 Buckypaper

One of the more promising avenues for carbon nanotubes is the development of buckypaper. This material is made from aggregates of carbon nanotubes and may be held together by a variety of methods. In the simplest case, buckypaper can be made by the acid

functionalization of the tubes and washing with deionised water. After drying, the tubes are suspended in a mixture of solvent and surfactant. A stable suspension is usually achieved after sonication and is then filtered and compressed. The advent of double-walled carbon nanotubes (DWCNTs) provided a means to create even stronger non cross-linked buckypaper due to the coaxial nature of the tubes, that is reflected in a higher stability when compared to SWCNTs. DWCNTs are in fact perfectly situated to provide the benefits of both SWCNTs and MWCNTs and this has been demonstrated by the production of strong flexible DWCNT buckypaper (Endo *et al.*, 2005). In this case, buckypaper was produced by sonicating 15 mg of DWCNT in 100 ml of ethanol for 30 mins. The suspension was then carefully poured onto a polytetrafluroetylene (PTFE) filter and dried for a period of 24 hours before being peeled off. It is important to note that the paper was produced without the use of a surfactant in order to increase the purity of the paper, and a quick but significant mention of the careful pouring with filtration to form the paper was made. This research highlights an important issue for the processability of CNTs. Is the application of technique equally or more important than the chemistry of cross-linking?

3.2 Photovoltaic devices

The addition of CNTs to organic photovoltaic (OPV) cells is of great interest due to the inherent properties of the tubes (Li *et al.*, 2010). Organic solar cells have garnered a lot of interest since the discovery of dye sensitized solar cells, and have been envisioned as a cheaper alternative to silicon based cells. The main drive behind the current research is to create a robust, flexible cell capable of sustaining many cycles as well as an increase in light absorption. One of the hurdles that need to be overcome is the relatively low carrier mobility that is found even in thin film organic polymers.

CNTs present and an attractive addition to thin film composites due to high charge mobility and extended conjugation and mechanical strength. SWCNTs provide an advantage to MWCNTs due to the diverse band gaps, which may be used to fine tune optical absorption, and reduce the effect of carrier scattering. Even with the advantages of SWCNTs in polymers, both SWCNTs and MWCNTs have been integrated into photovoltaic composites. These cells did improve the carrier mobility even when the doping level was low but the issue of solubility and processability still limits its potential efficiency. Another limitation is the combination of both the polymer donor and molecular acceptor in the same layers (bulk heterojunction design) which results in a highly disordered system with no clear phase boundaries (Yun *et al.*, 2008). One way to circumvent these issues is to follow an in situ polymerization method for a series of SWCNTs–poly[(2-methoxy,5-octoxy)1,4-phenylenevinylene] (MO-PPV) nanocomposites using different weight ratios. These are then cross-linked to acylated SWCNTs resulting in MO-PPV/SWCNTs nanocomposites with a defined interface (Fig. 10.). The result can be seen in the increase in electron mobility from the SWCNT to the polymer (Yun *et al.*, 2008).

Photoluminescence studies showed that there was significant quenching with the addition of SWCNTs, and further solid-state photoluminescence spectra of the thin films indicated that there was charge transfer from MO-PPV to SWCNTs. The MO-PPV/SWCNTs bulk molecular heterojunction solar cells produced exhibited an improvement in the efficiency which can be attributed to the nanophase separation which helps to not only enable carrier transport and exciton dissociation, but also reduce the recombination of photogenerated charge carriers in the thin films.

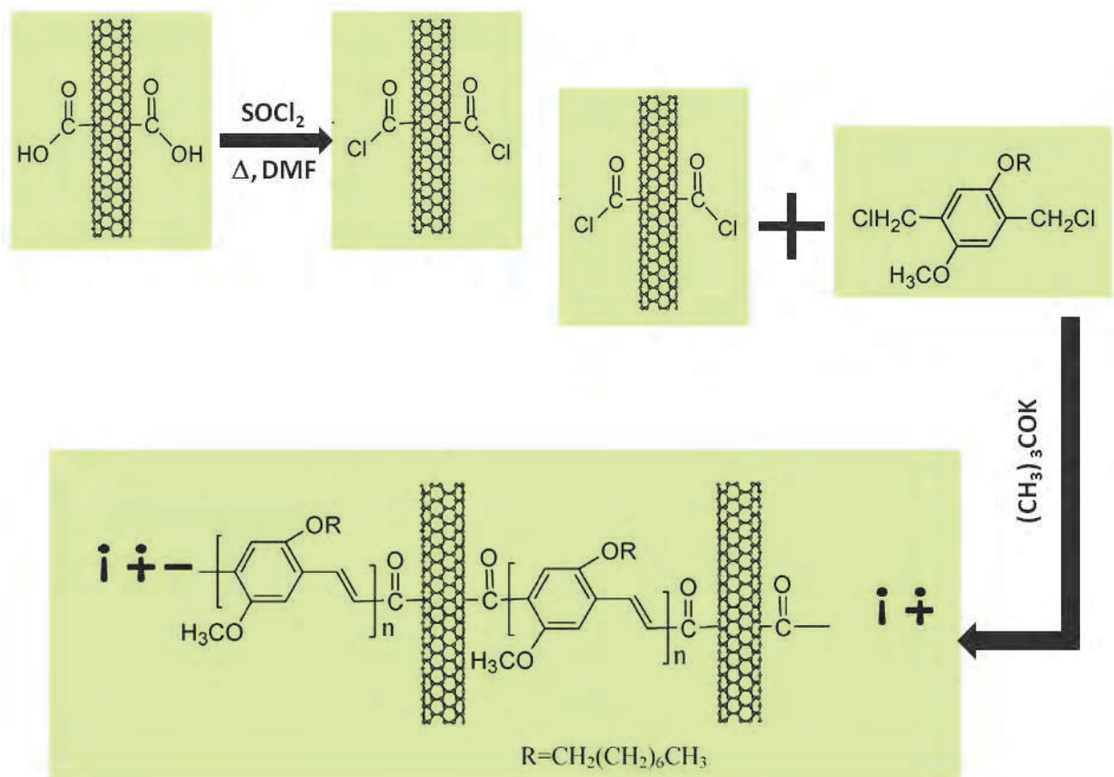

Fig. 10. Reaction scheme of the acylation of CNTs and the cross-linking of the tubes with MO-PPV. Figure adapted from (Yun *et al.*, 2008).

3.3 Artificial muscles

In the list of potential applications for carbon nanotube films, the nature of biological interactions is far more curious, following trends more commonly attributed to science fiction. One such concept is that of artificial muscles. The research into using CNTs as muscles has been ongoing with various noteworthy achievements of the last few years (Vohrer *et al.*, 2004). The work by Ray Baughman at the University of Texas has shown that cross-linking vertically aligned CNTs can produce a material with intriguing properties. The films act as CNT actuators and are produced from aerogel sheets which are drawn from forests of aligned carbon nanotubes (Aliev *et al.*, 2009). In this design, actuation, which is shown as a rapid spreading out of the width of the film after an insertion of charge, is followed by the contraction of the length of the film. The actuation across the length creates an isometric specific stress that can be up to 4.0 MPa cm^3/g. Mammalian skeletal muscle can typically withstand a stress of 0.1 – 0.35 MPa (Madden *et al.*, 2004), which in comparison to the isometric stress–generation capability of the sheet which was measured at 3.2 MPa, many times higher than the stress-generation capability of mammalian skeletal muscle.

The film is also being explored in relation to the behavior of the strain in extreme temperatures, and the advantages of controlling the structural changes. The research group highlight the possibility of tuning the density of the film for use in electrodes and light emitting displays.

4. Conclusion

In this chapter, we have discussed some of the successful approaches to cross-linking CNTs. For the formation of highly cross-linked CNT composites, the de-fluorination process is clearly an advantage. The fluorination of CNTs produces C_2F stoichiometries which translate across the surface of the tubes, and can be beneficial for further processing. The tubes can then be fully defunctionalized by thermal treatment producing volatile fluorinated carbonaceous molecules (CF_x). The resulting CNTs have active sites all over the surface.

For the formation of flexible thin films, the production of buckypaper or nanotubes mats from thiolated CNTs are possible and may serve to be good electrodes or sensors for future applications.

Although the characterization of the composites formed needs to be extensive, it is possible to prove the nature of interactions between the tubes and the cross-linker. It is clear that the recent Nobel Prize for the work on graphene is helping to stimulate interest in the field, with many aspects envision for carbon nanotubes being translated to novel graphene architectures. It is expected that for the immediate future, the research into graphene and CNTs will take a synergistic approach especially in the area of cross-linking. There is already some promising research available that explores the nature of cross-linking between the related graphene oxide sheets (Park *et al.*, 2009).

The application of artificial muscles really emphasizes the potential for the future of carbon nanotube research, demonstrating our ability to unlock the skills required to control nanoscale assembly.

5. Acknowledgments

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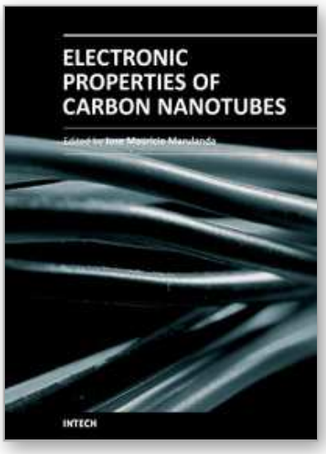

Electronic Properties of Carbon Nanotubes

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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. These one-dimensional (1D) graphene sheets rolled into a tubular form have been the target of many researchers around the world. This book concentrates on the semiconductor physics of carbon nanotubes, it brings unique insight into the phenomena encountered in the electronic structure when operating with carbon nanotubes. This book also presents to reader useful information on the fabrication and applications of these outstanding materials. The main objective of this book is to give in-depth understanding of the physics and electronic structure of carbon nanotubes. Readers of this book should have a strong background on physical electronics and semiconductor device physics. This book first discusses fabrication techniques followed by an analysis on the physical properties of carbon nanotubes, including density of states and electronic structures. Ultimately, the book pursues a significant amount of work in the industry applications of carbon nanotubes.

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