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Brownlie, L., & Shapter, J. (2018). Advances in carbon nanotube n-type doping: Methods, analysis and applications. *Carbon*, 126, 257–270. <https://doi.org/10.1016/j.carbon.2017.09.107>

which has been published in final form at

<http://dx.doi.org/10.1016/j.carbon.2017.09.107>

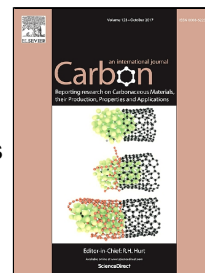
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Accepted Manuscript

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PII: S0008-6223(17)30991-0
DOI: 10.1016/j.carbon.2017.09.107
Reference: CARBON 12437
To appear in: *Carbon*
Received Date: 09 August 2017
Revised Date: 23 September 2017
Accepted Date: 30 September 2017

Please cite this article as: Liam Brownlie, Joseph Shapter, Advances in Carbon Nanotube n-type Doping: Methods, Analysis and Applications, *Carbon* (2017), doi: 10.1016/j.carbon.2017.09.107

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Advances in Carbon Nanotube n-type Doping: Methods, Analysis and Applications

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Abstract

Great advances in semiconductor technologies continue to be made with the demand for cheap, non-toxic, easily processed and environmentally friendly technologies on the rise. Single-walled carbon nanotubes (SWCNTs) are viewed as a promising candidate that satisfies these criteria however proper doping of the SWCNTs to provide n-type behaviour has been a persistent issue. In recent years, great advances have been made in providing air stable and efficient n-type doping of SWCNTs. This review presents the most recent and promising methods of n-type doping SWCNTs highlighted for their simplicity and quality of electrical properties. The analysis and major applications of these semiconductors with a focus on thermoelectric devices and transistors are discussed.

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1. Introduction to Carbon Nanotubes

1.1. A History of Carbon Nanotubes

First definitively observed in 1991 [1] during a period of intense interest in fullerenes and other carbon materials, carbon nanotubes (CNTs) were quickly recognised as a material with huge potential for a variety of applications. Early on, much of the interest in CNTs was in gaining an appreciable understanding of the structure, properties and growth methods [2-7].

It is common when discussing CNTs to cite the work of Iijima [1] as the discovery of the carbon nanotube. However the work that laid the foundation for their discovery can be dated back much further, to 1889 to be precise where a patent proposing the use of carbon filaments grown through thermal decomposition of methane in light bulbs was filed by Edison [8]. This and other pieces of supporting evidence from before Iijima's 1991 publication could also be credited as 'the discovery of the carbon nanotube'.

After Iijima's 1991 publication CNTs quickly established themselves at the forefront of carbon material technology with many scientists eager to test various hypotheses to truly probe the limits of the CNTs' capabilities. The plethora of information gathered about the properties, growth and applications allowed many scientists to 'streamline' their interest in nanotubes. Even after this focus a large number of CNT applications are still being

investigated, many of which will not be mentioned in this review which instead will focus on the methods, analysis and applications of n-type doping CNTs.

As a result of their semi-conducting behaviour single-walled CNTs have become an increasingly interesting prospect for use in solar cells, transistors and thermoelectric devices among other applications. This semi-conducting behaviour has become an inspiration for scientists wanting to optimise and design hybrid or indeed fully organic electronic devices. The issue with this is that semiconductor electronics require the use of both p- and n- type semiconductors. The p-/n- behaviour of semiconductors may be controlled through doping of the semiconductor with either electron-donating or electron-withdrawing dopants depending on which behaviour is desired. P-doping of semiconducting carbon nanotubes is rather simple and requires very little effort as the CNTs will naturally adsorb molecular oxygen from the environment [9]. The addition of the electron withdrawing oxygen causes the CNTs to exhibit p-type behaviour. While p-type doping of CNTs is easy, n-type doping of CNTs has proven to be much more challenging in terms of the doping stability and overall performance of the devices. The purpose of this review is to examine the most recent work published in this field with the aim of achieving the n-type CNT doping goal for various applications.

2. N-type doping of CNTs

N-type doping of single-walled CNTs (SWCNTs) has attracted a lot of attention in recent years as the demand for environmentally friendly, non-toxic, easily processed and cheap materials with desirable electrical characteristics has increased. The promise of a cheap, fully organic electronic device is extremely desirable in many areas however before defining these areas, n-type doping must first be discussed in a broader sense.

N-type doping of SWCNTs allows the customization of nanotube properties through the addition of electron donating dopants. Specifically, it ensures that when applied in a given heterojunction, the nanotubes will have no desire to draw electrons from the opposing side of the junction as this craving is sated by the electron donating dopant. Instead, the nanotube will now be more likely to 'give up' its electrons to the p-type side of the heterojunction leaving behind an electron vacancy (hole) in the nanotube that is stabilised by the excess of negative charge carriers provided by the dopant.

The main issue with n-type doping SWCNTs is in the longevity of the n-type behaviour. There has been a large amount of work into developing stable n-type doping methods that

optimise the lifetime of the nanotube's n-type behaviour. These methods include polymer wrapping [10, 11], encapsulation of organometallic materials within the nanotubes [12, 13], and more recently doping by salt anions with counter cations has been shown to be successful [14]. The main factor affecting the longevity of n-type nanotube doping is oxidation by atmospheric oxygen adsorbing onto the doped nanotube [13]. As a result, the quality of n-type nanotube doping is considered not solely by its electrical properties but also by its air stability.

2.1. Methods of n-type Doping

The stability of n-type dopants has been seen to vary widely depending on the dopant with efforts still being taken to determine the most environmentally durable dopant. For instance, work conducted in 2012 into the fabrication of air-stable thermoelectric modules using p- and n- type nanotubes addressed this issue [10]. This work n-type doped SWCNTs through a combination of polyethyleneimine (PEI) and sodium borohydride (NaBH_4). Single walled CNTs were dispersed in water with sodium dodecylbenzenesulfonate introduced as a surfactant. Un-doped nanotubes were filtered onto a polytetrafluoroethylene (PTFE) membrane and acted as the control. NaBH_4 doping was achieved by immersing a CNT coated PTFE membrane in 1M NaBH_4 solution while PEI doping was achieved by adding PEI to the nanotube dispersion to a 5wt% concentration. The PEI dispersion was then left for a pre-determined period of time before being filtered onto a PTFE membrane. Combined NaBH_4 and PEI doping was achieved through immersing PEI doped CNT films in 1M NaBH_4 solution.

PEI is known to irreversibly adsorb to SWCNTs providing n-type behaviour for a relatively short period of time [10, 11] and while the method for this wrapping is simple, the n-type behaviour does not have sufficient lifetime to make it a long term solution. The monolayer like wrapping of CNTs by PEI was discussed in this work however any effect the surfactant may have on the efficiency of this wrapping is not [10]. Suffice it to say, due to its size and proximity to the nanotube, the surfactant may have blocked binding of the PEI to some extent thus limiting the space in which PEI may adsorb to CNTs and promote the desired n-type behaviour. This in turn would lead to more 'open' space on the nanotube where atmospheric O_2 may adsorb and cause a reversal in nanotube semiconducting behaviour.

The reduction of the CNTs by NaBH_4 both on its own and in conjunction with the PEI wrapping is an elegant solution to the n-type doping problem [10]. Indeed, the combination of nanotube reduction and polymer wrapping provided the best n-type characteristics returning a thermopower of $-77\mu\text{V.K}^{-1}$ representing a clearly superior result compared to the $-57\mu\text{V.K}^{-1}$ and $-24\mu\text{V.K}^{-1}$ thermopowers recorded for the singly treated PEI and NaBH_4 samples respectively. Thermopower is a measurement commonly applied in the field of thermoelectrics and is more commonly known as the Seebeck coefficient. This value refers to the electrical voltage induced by a temperature difference across a material. In general, it represents the amount of electricity produced from heat. The sign of the Seebeck coefficient is indicative of the semiconducting nature of the material, where an n-type semiconductor will have a negative Seebeck Coefficient due to the negative charge carriers in the material (electrons). Conversely, a p-type semiconductor will possess a positive Seebeck coefficient as it possesses positive charge carriers (electron holes). The Seebeck coefficient will be discussed throughout this review in reference to other work as it is a common doping 'quality' indicator and is useful for tracking the behaviour of the n-doped CNTs for thermoelectric devices.

In general, methods of reducing CNTs to provide n-type behaviour have been growing in popularity in recent years as they have shown promising n-type characteristics, including large Seebeck coefficients and long doping lifetimes. One such method that has been particularly successful is achieved through doping CNTs by reduction via hydroxide or halide anions followed by charge stabilisation through the presence of tetraalkylammonium (R_4N^+) cations or crown ether complexes with cationic alkali ions [14].

This work looked into using simple salts with crown ethers as new doping materials to n-type dope SWCNTs. Experimentally this process is rather simple. All that is required is immersion of the CNT film to be doped into a 0.1M salt and crown ether solution in methanol. Tetraalkylammonium salts were also tested as dopants through CNT immersion in equivalent solutions [14]. Y. Nonoguchi et al. investigated solvent effects on doping by tetramethylammonium hydroxide and found aprotic solvents to be the most effective doping solvents based on the resultant Seebeck coefficient. This solvent dependence is better understood when considering the mechanism by which the CNTs are doped in this process. The doping mechanism is similar for each of the materials studied in this work but we will only discuss the crown ether-salt complex mechanism as it was

these systems that showed the most desirable n-type characteristics [14]. Various salts were applied however none simpler perhaps than NaOH. In this example, the sodium cation will 'seek out' the crown ether and complex in its centre where its charge is stabilised by the lone pairs of the oxygen molecules. The hydroxide on the other hand will undergo an oxidation reaction to form hydrogen peroxide (H_2O_2). This oxidation is achieved through reduction of the CNTs present in the system. The OH^- anions undergo an electron transfer reaction with CNTs before binding together to form H_2O_2 thereby reducing the CNT and leaving it negatively charged. This negative charge then encourages the cationic crown ether complex towards the nanotube through electrostatic attraction although it does not bind, it merely stabilizes the negative charge. This process covers the negative charge carriers that now provide the CNTs with their n-type behaviour. The large crown ether complexes likely block adsorption of atmospheric O_2 improving the n-type lifetime of the CNTs either through electrostatic rejection by the oxygen present in the crown ether or by simple physical blocking.

In terms of performance, the nanotube films were tested at a variety of temperatures, including upwards of $100^{\circ}C$ and retained their n-type behaviour for over 600 hours when KOH and benzo-18-crown ether were used. This coupled with Seebeck coefficients consistently more negative than $-30\mu V.K^{-1}$ show this method of n-type doping to be a promising method for future applications.

One of the most recent reports into n-type doping of SWCNTs for thermoelectrics applied organic nanoparticles to n-type dope the SWCNTs. Y. Nonoguchi et al. set out to n-type dope SWCNTs with triphenylmethane carbinol base (TPM-CB) nanoparticles. TPM-CB is the base form of malachite green. The researchers' choice of malachite green is due to its high reduction power and its use in early organic photovoltaic PN junction devices [15]. The high reducing power of malachite green indicates its electron donating ability, a pivotal feature of potential n-type dopants. Malachite green possesses a positive charge that is able to resonate throughout its structure. While this would not prevent its use as an n-type dopant, the doping it provides is limited [15]. This is likely due to malachite green's hindered ability to undergo an electron transfer reaction in its cationic state. Electron transfer reactions between dopant and SWCNT are key to n-type doping and are discussed in many papers on this subject [13-28]. In its basic form, TPM-CB, possesses no such positive charge and is thus able to undergo electron transfer reactions with the nanotubes through both of its amine chains (Fig. 1).

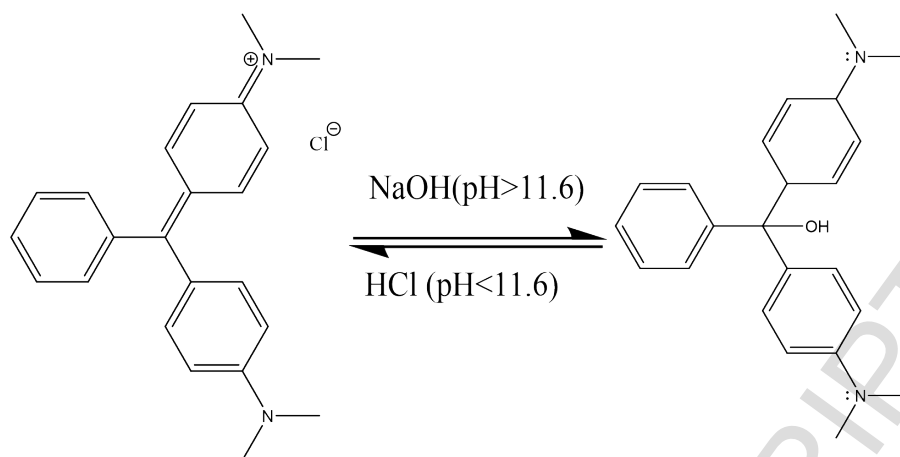


Figure 1: pH governed conversion of malachite green to TPM-CB.

In any case, Y. Nonoguchi et al. show conclusively the advantage of using the TPM-CB form over regular malachite green through the thermoelectric experiments conducted after doping with each species [15]. It was found that while malachite green did partially n-type dope the SWCNTs, it wasn't capable of switching the semiconducting behaviour dramatically enough. This is shown in the Seebeck coefficients obtained after doping. These experiments showed malachite green doping provide Seebeck coefficients around $-2.5\mu\text{V.K}^{-1}$ which is not substantial enough to be particularly useful [15]. However, doping with TPM-CB did drastically alter the Seebeck coefficient, and hence the semiconducting behaviour, shifting the coefficient to $-59\mu\text{V.K}^{-1}$ from the $36\mu\text{V.K}^{-1}$ for the pristine SWCNTs. In addition, the stability of this doping in air is very high with consistent n-type behaviour measured over an 800 hour period [15].

The major feature of this work however is in the method by which they achieved the n-type doping of SWCNTs and the pH dependence thereof. The method used by Y. Nonoguchi et al. is elegant in its simplicity and efficient in its end results. It involved submerging bucky paper in aqueous malachite green solution for 17 hours. This solution was pH controlled to allow the TPM-CB to form in situ. The organic nanoparticles used for doping in this work are formed by exploiting this in situ formation. TPM-CB is insoluble in water and as such will precipitate out of solution under basic conditions [15]. The so-called 'transition pH' where malachite green 'transitions' to TPM-CB occurs at a pH of approximately 11.6 [15] and while the structural change in basic solution is well recorded in literature, some literature indicates this structural change is 'transitional' at a lower pH [19, 20].

In any case, immersing self-standing SWCNT sheets (bucky papers) in aqueous basic malachite green solution for 17 hours seemed sufficient to dope the SWCNTs with organic nanoparticles as shown by SEM and Energy Dispersive X-ray (EDX) elemental analysis. This showed 50-200nm spherical, nitrogen containing particles present on the SWCNTs making up the bucky papers (Fig. 2). The formation of these particles is down to the ‘transition’ of malachite green to TPM-CB at pH 12 which is gradual enough to promote only slight aggregation of TPM-CB so as to form the organic nanoparticles necessary. It was found that increasing the pH too much, making the solution too basic, would in fact decrease the quality of doping which likely indicates too much aggregation of TPM-CB at this pH meaning larger particles and thus less SWCNT contact within the pores of the bucky paper [15].

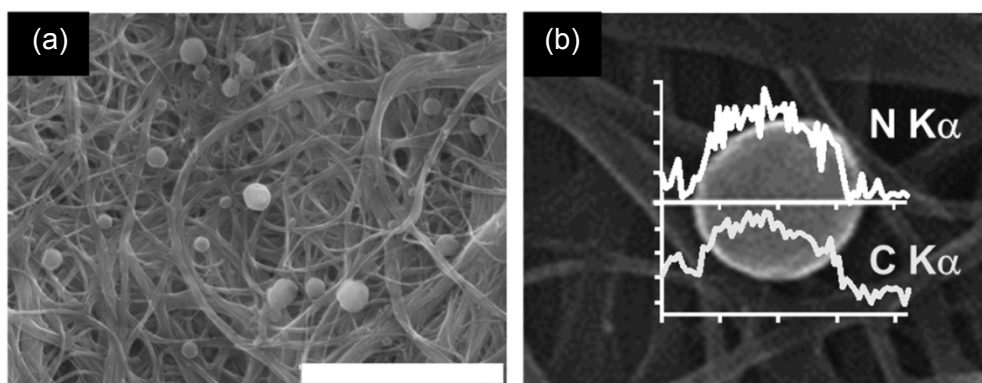


Figure 2: (a) SEM image of organic nanoparticle-SWCNT composite and (b) EDX elemental analyses of a single organic nanoparticle. Reproduced from [15] Copyright (2016) with permission from John Wiley and Sons.

This work shows promise for a simple and effective method of n-type doping SWCNTs that provides highly desirable thermoelectric properties with Seebeck coefficient measurements consistently ‘higher’ than $-40\mu\text{V}/\text{K}$ over a recorded 800 hour period.

2.2. Chemical Doping

SWCNTs have been used in chemical reactions for a number of years and over that time they have been used in a number of roles. Undoped SWCNTs have predominantly been applied as supports for catalysts [29-31] but have also been shown to possess their own catalytic capabilities [32-34]. The SWCNT’s catalytic ability may be supplemented through doping to enhance their capabilities within certain reactions. Nitrogen is a dopant commonly used to this end, and while the semiconducting properties of the SWCNTs are not relevant in this context, this doping would most certainly lead to n-type behaviour.

Much of the literature in this space refers to nitrogen (N-doping) or Boron (B-doping) doping of SWCNTs to affect their performance in chemical reactions. Nitrogen doping is the more popular of the two however B-doping has been used to provide an electrocatalyst for oxygen reduction reactions [35] and caused some speculation as to whether boron and nitrogen co-doping may be useful [36]. In any case, N-doping has been shown to apply to a variety of reactions including: oxygen reduction reactions [37-42], hydrogen evolution reactions [43], and biological reactions [44]. Additionally N-doped SWCNT electrocatalysts have been applied in biosensing [45].

Most recently N-doped SWCNTs have been used to support palladium nanoparticles to assess their catalytic abilities within the Heck reaction and in the oxidation of benzyl alcohol [41]. L-L. Wang et al. adsorbed Pd nanoparticles to the walls of N-doped SWCNTs. SWCNTs were chosen due to their popularity as catalyst supports. This popularity stems from the SWCNT's high specific surface areas and thermal stabilities among other desirable properties. Most important for L-L. Wang et al. is the environmental acceptability of the SWCNTs as they aimed to design a 'green' synthesis of Pd/N-doped SWCNT catalysts [41]. SWCNTs are themselves able to be used as catalysts or catalyst supports without modification. It has been reported by L-L. Wang et al. and others [46-50] that doping them with nitrogen alters their abilities in these applications.

The N-doped SWCNTs synthesis method applied by L-L. Wang et al. used CVD applying an Fe-containing SBA-15 molecular sieve as the catalyst and using ethylene diamine as the nitrogen and carbon source for nanotube growth [41]. The synthesis of the Pd/N-CNTs is rather simple where the N-doped SWCNTs are dispersed in sodium dodecyl sulfate (SDS) solution in ethylene glycol by sonicating for 3 hours. Polyvinylpyrrolidone(PVP) is then added and the dispersion is allowed to stir at 60°C for 15 minutes before the dropwise addition of H_2PdCl_2 in ethylene glycol solution. The reaction is then left at 130°C for 2 hours to allow the Pd/CNT catalysts to form [41]. The ratio of H_2PdCl_2 to N-doped SWCNT is changed to allow the effect of loading on the N-doped CNTs to be established.

SEM and TEM were used to confirm the success of Pd adsorption to the N-doped SWCNTs in addition to determining the effect SDS and PVP have on the synthesis. The SEM images taken confirm attachment of Pd to the N-doped SWCNTs in the presence of

PVP and SDS with an absence of PVP causing aggregation of the Pd with a small portion being deposited on the SWCNTs in random fashion [41] (Fig. 3). Figure 3(d-f) show the significant impact PVP has on the distribution of Pd over the N-doped SWCNTs with much smaller aggregations and more uniform spreading of Pd is seen at PVP:Pd ratios of 2.5:1 and 10:1 with larger aggregations seen at the higher ratio. L-L Wang et al. do identify an optimal PVP:Pd ratio of 5:1 as represented in Figure 3(e) which shows a uniform and even distribution of Pd nanoparticles across the surface of the N-doped SWCNT with very little aggregation. Although not discussed by L-L. Wang et al., PVP is commonly used to stabilise Pd nanoparticles due to coordination of the C=O group of the PVP to the Pd nanoparticles [51-54]. It is possible the 5:1 PVP:Pd ratio is sufficient to efficiently protect and separate the Pd nanoparticles whereas addition of more PVP simply causes aggregation of the polymer with the Pd nanoparticles. Whilst at lower ratios there is not enough PVP to separate all of the Pd nanoparticles such that they may evenly spread across the N-doped SWCNTs.

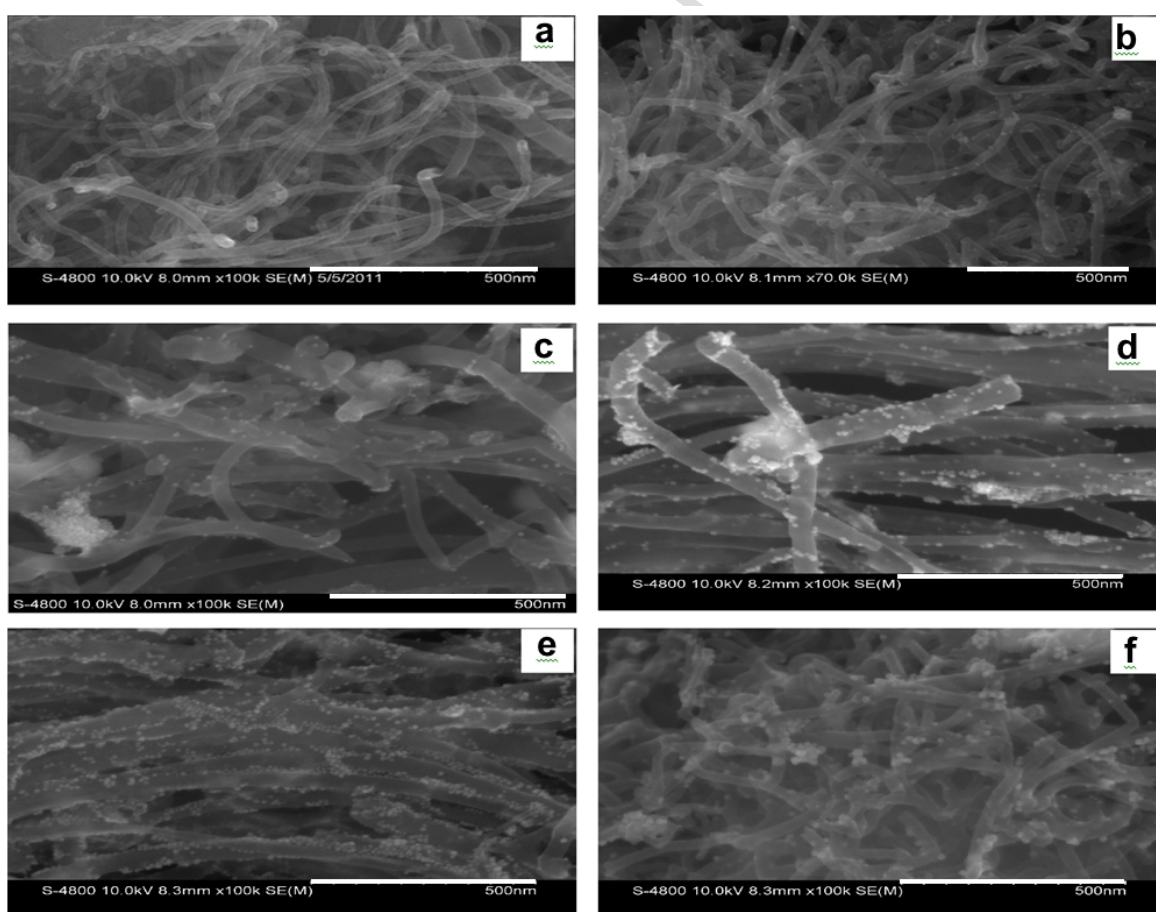


Figure 3: SEM images of (a) N-doped SWCNTs, (b) PD/N-doped SWCNTs synthesised without SDS/PVP, (c) PD/N-doped SWCNTs synthesised without SDS, (d) PD/N-doped SWCNTs synthesised with PVP:Pd ratio 2.5:1, (e) 5:1, (f) 10:1. Reprinted from [41] Copyright (2017) with permission from Elsevier.

The catalytic performance of the Pd/N-doped SWCNT catalysts was tested by L-L. Wang et al. initially in the Heck reaction of iodobenzene. The reaction was seen to readily take place at temperatures between 50°C and 130°C with a conversion of 92.8% reported at 50°C. Additionally, short reaction times of 1hr at 100°C or 0.5hr at 130°C afforded nearly 100% conversion [41]. It was seen that higher wt% concentration of the Pd/N-SWCNTs afforded higher conversion percentages with 74.2% and 99.9% conversion recorded for 4.8wt% and 8.6wt%, respectively. For reference other methods of catalysing the Heck reaction have shown less than 90% conversion over a 3hr period [55] showing this to be an improvement on conventional catalysis methods for the Heck reaction.

The solvent-free aerobic oxidation of benzyl alcohols was also used to test the Pd-N-doped SWCNTs catalytic abilities where an improved conversion was seen with an increase in Pd nanoparticle loading showing the catalysis to be dominated by the palladium and not so much down to the presence of the N-doped SWCNTs [41]. Both Pd/N-doped SWCNTs and Pd/SWCNTs were tested using this reaction and 90.7% conversion was observed for the N-doped case at an 8.6wt% concentration. Whilst the Pd/SWCNTs gave a lower conversion of approximately 50% at a 9wt% concentration. This indicates the doping of SWCNTs with nitrogen has a significantly positive effect on the catalytic ability of nanotube supported catalysts.

Another example of the use of n-type (N-doped) SWCNTs in catalysis looked at N-doped SWCNTs as a metal-free catalyst rather than a catalyst support as L-L. Wang et al. did [41]. The N-doped SWCNTs synthesised by K. Aoki et al. [42] were manufactured through dielectric barrier discharge in high pressure nitrogen instead of the conventional CVD method. It was reported that this growth method led to higher nitrogen surface concentrations than the CVD method [42]. The main purpose behind this work was to assess the capabilities of N-doped SWCNTs in catalysing an oxygen reduction reaction (ORR) and the spatial distribution of nitrogen with the N-doped nanotubes.

Although not discussed until this point the incorporation of nitrogen into the CNT structure causes some interesting changes to the CNT structure. It has been observed that the incorporation of nitrogen into the nanotube structure promotes a bamboo-like structure for the nanotubes [41, 42, 56]. TEM, EDX, EELS and XPS have been used to characterise the N-doped CNTs. TEM showed most clearly the bamboo-like structure of

the N-doped CNTs as displayed in Figure 4 where small ‘ridges’ can be observed along the nanotubes.

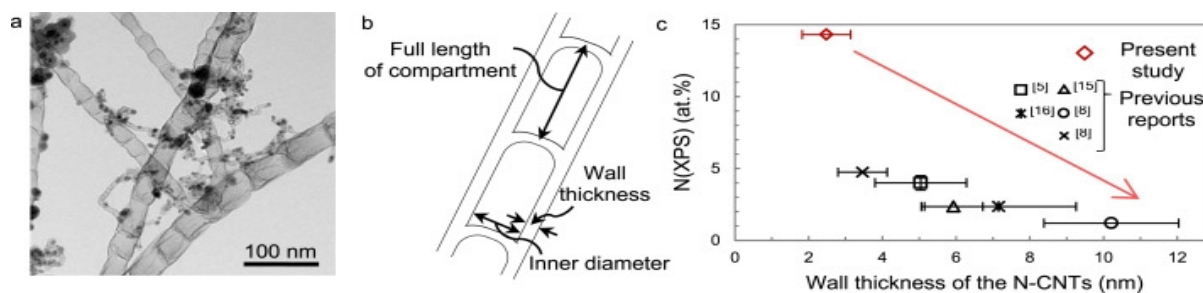


Figure 4: (a) TEM image of Bamboo-like N-doped CNTs (b) Schematic of N-doped CNT dimensions (c) Comparison of N concentrations vs other methods [39, 57-59] plotted against wall thickness. Reproduced from [42] Copyright (2017), with permission from Elsevier.

EELS provided a more detailed elemental map from which the distribution of nitrogen throughout the nanotube structure could be determined. It can be seen in Figure 5 that the majority of nitrogen exists on the fringes of the compartments (Fig 4b.) with the highest concentrations found in the curves of each ‘node’.

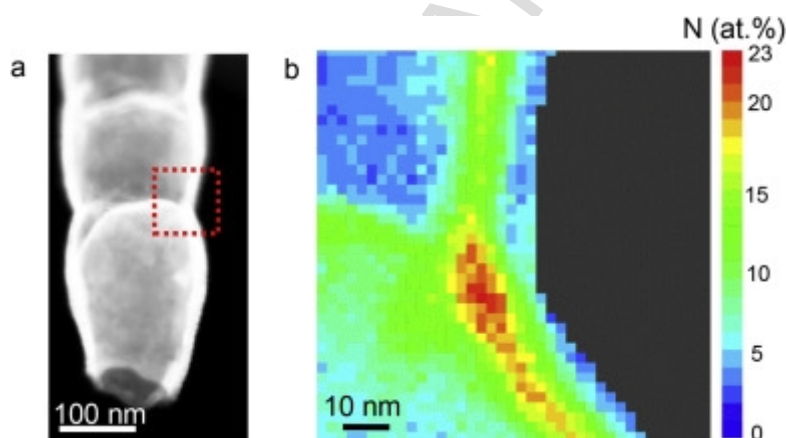


Figure 5: (a) Scanning TEM image of bamboo-like N-doped CNT, EELS region marked (b) Nitrogen mapping over N-doped CNT. Reproduced from [42] Copyright (2017), with permission from Elsevier.

In terms of the catalytic ability of K. Aoki et al.’s N-doped CNTs have a trend of higher onset potential with higher nitrogen concentrations, as has been seen previously. However, this work reports the highest ORR onset potential and pyridine-like nitrogen concentration in comparison to CVD grown N-doped CNTs [39, 57, 58, 60, 61] (Fig. 6). In cathodic electrochemical reactions i.e. reaction at the cathode, the onset potential is defined as the highest potential at which product is formed [62] thus the higher the onset potential the wider voltage range the reaction has to operate thus improving its yield. The

onset potential is also used as a measure of catalytic ability by simply comparing identical reactions using different catalysts [63].

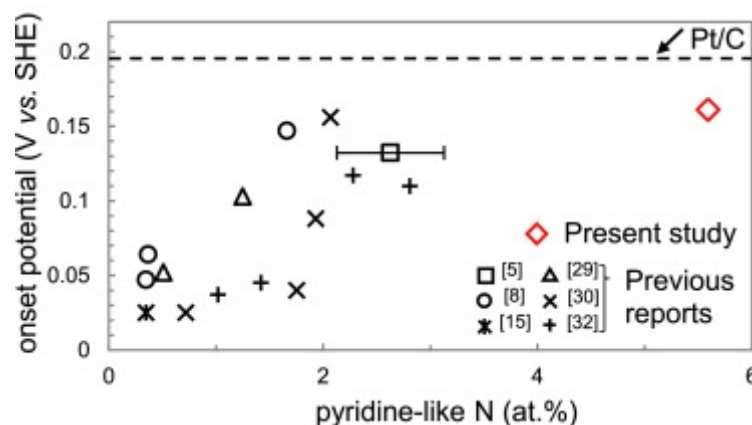


Figure 6: Onset potential as a function of pyridine-like nitrogen concentration. Reproduced from [42] Copyright (2017), with permission from Elsevier.

In any case, this work represents a novel method of synthesising N-doped CNTs with high catalytic activity. It also provides much needed structural information on N-doped CNTs which will be beneficial in the development of further metal-free catalysts using N-doped CNTs.

3. Analysis of n-type CNTs

Due to the various functionalisation and modifications available to n-type doped CNTs it is important that there are common methods of characterisation available to confirm successful functionalisation to support any measurements taken of the CNT's now n-type behaviour. The methods conventionally used include: Scanning Electron Microscopy (SEM) [10, 15, 64], Transmission Electron Microscopy (TEM) [41, 42], Raman Microscopy [10, 13, 14, 65] and X-Ray Photoelectron Spectroscopy (XPS) [13, 15, 65].

3.1. Scanning Electron microscopy

SEM is a popular method for imaging CNT films deposited on substrates. As such is it a natural 'port-of-call' for those modifying CNTs with various functionalisations that may alter the CNT films formed. For instance, C. Yu et al. conducted an SEM study on CNT films modified with PEI to provide the desired n-type behaviour [10]. In this study, PEI-CNT films were directly compared to pristine CNT films to ascertain any differences between the two films. Wrapping the relatively thin CNTs in a viscous polymer such as PEI (MW ~600) would theoretically fill in many of the 'gaps' in the film and this is what was observed. Direct comparison of SEM images taken of two CNT films on

polytetrafluoroethylene (PTFE) membranes showed significant differences in the film on addition of the PEI dopant. Prior to doping, the film appears to be largely made up of long straight nanotubes, as would be expected. However, introduction of PEI into the system caused changes in the CNTs forcing them to curl as a result of being wrapped by the polymer [10]. This effect is displayed in Figure 7.

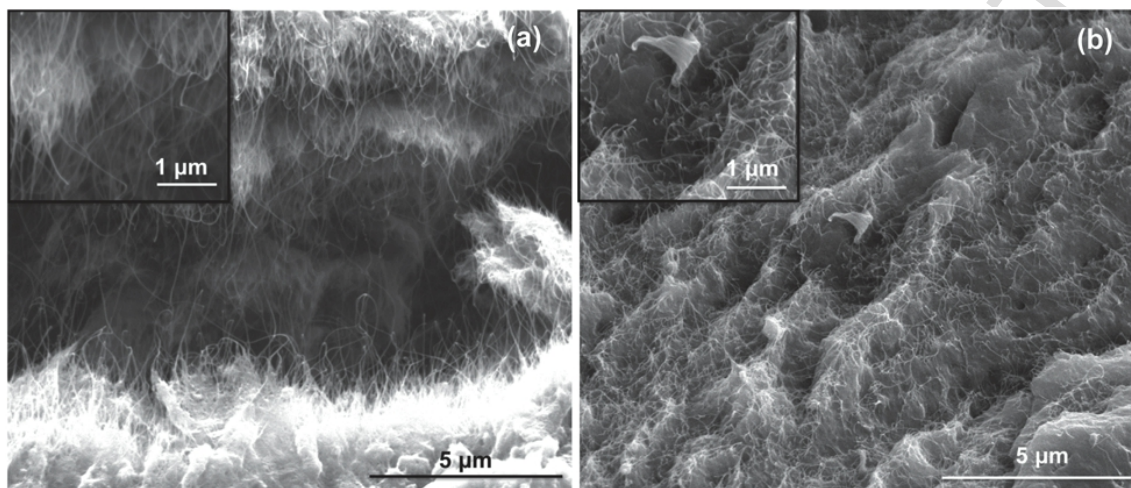


Figure 7: Cross-sections of (a) pristine SWCNT film and (b) PEI doped SWCNT films. Reproduced from [10] Copyright (2012), with permission of The Royal Society of Chemistry.

3.2. Raman Spectroscopy

Raman is another popular technique for the analysis of nanotubes due to the distinctive Raman spectrum for CNTs. This spectrum as well as its component peaks provides a large amount of information on the properties of the nanotubes under inspection. A typical CNT Raman spectrum is shown in Figure 8.

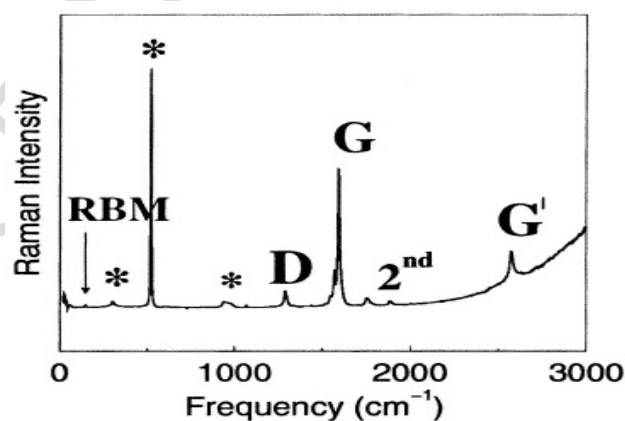


Figure 8: Typical Single-walled CNT Raman Spectrum. Reproduced from [66] Copyright (2002), with permission from Elsevier.

Each peak in the Raman spectrum gives specific information on different aspects of the nanotubes under inspection. Much of the information is contained within the D, G, G' and RBM bands. The D band is in effect the 'defect' band of the nanotube Raman spectrum and is an indicator of anything that detracts from the 'constant' sp^2 hybridisation of the carbon atoms in the nanotube's 'quasi-infinite lattice' [67]. In general the more defects that exist within the nanotube lattice, the higher the D-band intensity will be. The G-band on the other hand is an intrinsic vibration specific to carbon materials assigned to the vibration of carbon atoms at the surface of the nanotube [68]. This G-band therefore makes a good reference point when using Raman to qualify the level of defects present in a nanotube sample. This is done through taking a ratio of the D and G bands. The G' band is a second-order overtone of the D vibration [69] which is why it is often referred to as the 2D band, both G' and 2D are acceptable terminology for this band. The RBM band represents the Radial Breathing Mode of the nanotube. This Raman signal is specific to SWCNTs and will not appear in the Raman spectra of other materials [70]. The RBM may be thought of as a periodic expansion and contraction of a cylinder (SWCNT).

Raman spectroscopy has shown itself to be a useful technique for monitoring nanotube modifications through observing changes in the nanotube's various bands that would indicate some change to the nanotube structure. Such observations have been used to support successful n-type modification in literature [13, 14, 65, 71-73].

One such study investigated the mechanism by which SWCNTs may be doped with nitrogen and the impact on the electronic properties and growth selectivity of the SWCNTs thereof [65]. Although not specifically investigated in this work the doping of SWCNTs with nitrogen would promote an n-type semiconducting behaviour for the SWCNTs. The SWCNTs were grown via a Chemical Vapour Deposition (CVD) process. The standard CVD method required exposing reduced metal oxide catalysts to acetylene on a silicon surface. However the change made by H. M. Barzegar et al. was to add ammonia (NH_3) along with acetylene at the growth stage [65]. The ammonia content was varied to achieve different levels of nitrogen doping in each SWCNT sample. XPS and Raman were used to analyse the success and effect of nitrogen doping the SWCNTs [65]. Raman spectra were taken of each N-doped SWCNT sample and as would be expected the RBM, D, G and G' bands were easily identified however various differences between the spectra were also observed. Firstly, The D:G ratio method, briefly described earlier, may be repurposed to provide information on SWCNT doping. A nanotube defect can be

thought of as anywhere on the nanotube where there is not sp^2 hybridised carbon as a ‘perfect’ CNT should consist of solely sp^2 hybridised carbon. Thus when a dopant is added to the nanotube structure some of it may adsorb but some may bond, causing sp^3 hybridised carbon to appear and thus contribute to the defect level and by extension the D-band intensity. Thus a larger D:G ratio, or lower G:D ratio, than an unmodified SWCNT sample would indicate successful doping of the SWCNT. This trend was exactly what was observed by H. M. Barzegar et al. who report a linear decrease in G:D ratio with increasing ammonia content indicating successful addition of the NH_3 to the nanotube structure as displayed in Figure 9(b) [65].

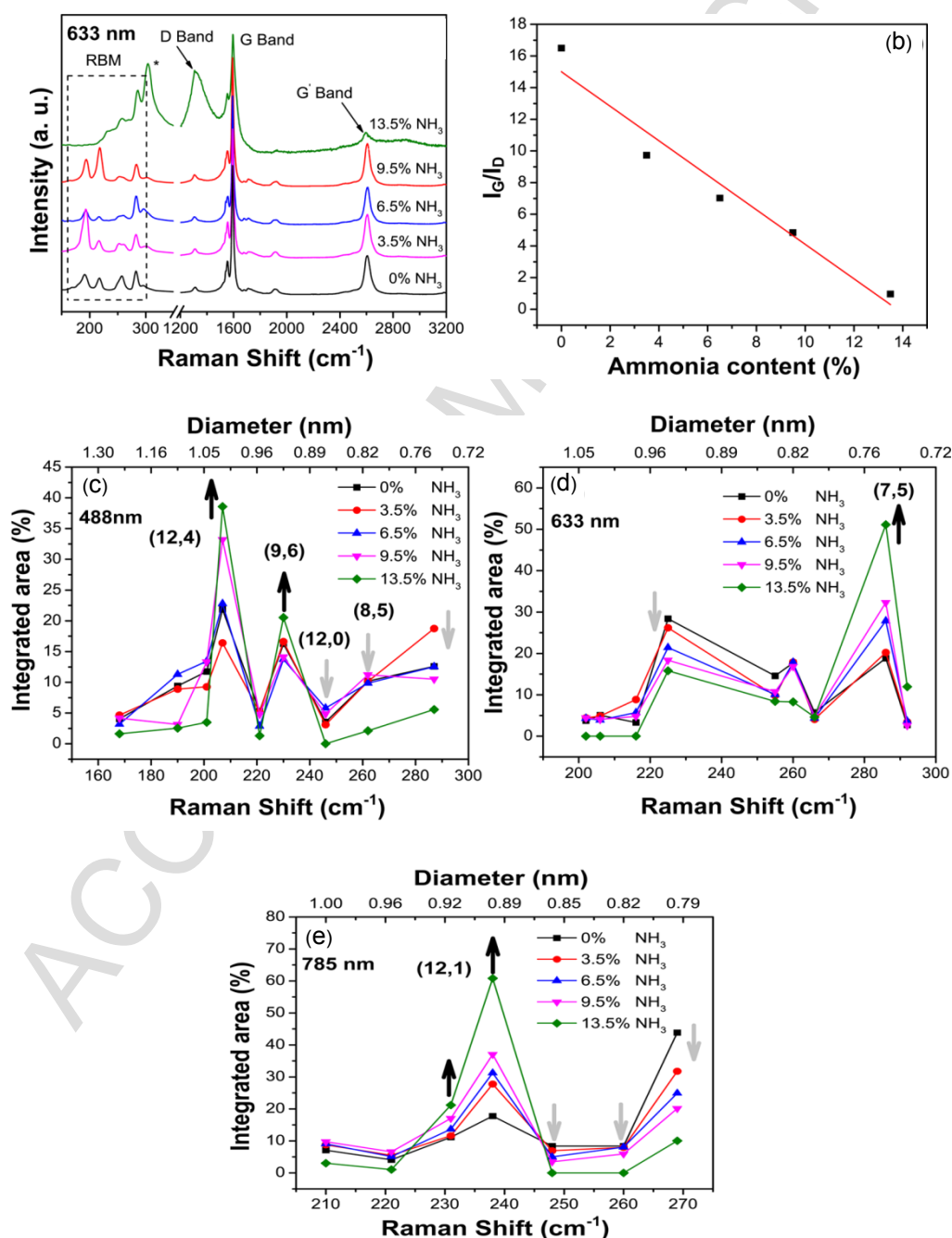


Figure 9: (a) Raman spectra of CNTs grown at varying ammonia feed percentages. (b) Ratio of G-band to D-band intensities at varying ammonia feed percentages. (c-e) Integrated area of RBM at varying ammonia feed percentages recorded by 488, 633 and 785nm excitation wavelengths respectively. Reproduced from [65] Copyright (2013), with permission from the American Chemical Society.

One of the main points of investigation for this work was the effect N-doping had on the growth selectivity of the SWCNTs. Intensity changes in the multiple signals present within the RBMs of the various nanotube samples as shown in Figure 9(c-e) indicates growth of specific SWCNT chiralities are preferred at some ammonia concentrations than others indicating the possibility for N-doped SWCNTs to grow with a selected chirality [65]. As a sidenote, suppression of the RBM can also be used as a successful doping indicator as adsorption of various larger dopants, such as PEI, can hinder the ‘inward-outward’ vibration related to the RBM signal.

3.3. X-Ray Photoelectron Spectroscopy (XPS)

In the context of n-type SWCNT modification, XPS is an invaluable technique for determining the success of a particular doping method. For instance, doping SWCNTs with nitrogen containing dopants is, as discussed, one of the more popular methods of n-type modification. To put this in perspective, SWCNT samples should not contain nitrogen if they are ‘pristine’ as they are commonly analysed on silicon substrates so carbon and some oxygen, usually from substrate oxidation, should be the only signals observed. So, doping with a nitrogen containing material would cause a nitrogen signal to be present in the nanotube XPS if the doping was successful.

XPS has been used to study successful n-type doping by a number of research groups [12, 15, 65]. In particular, XPS has been used as an analytical technique to study n-type doping from within the nanotubes rather than the polymer or salt adsorption methods discussed previously. T. Fukumaru et al. [12] endeavoured to encapsulate cobaltocene inside SWCNTs in order to achieve n-type behaviour. In this work XPS was used simply as a tool for cobalt qualification, where spectra of a pristine and an encapsulated cobaltocene SWCNT sample were directly compared to confirm cobalt only appeared after the necessary treatment [12].

The XPS spectra obtained in this work (Fig. 10) showed the success of cobalt encapsulation within the SWCNTs with the appearance of peaks at 781eV and 797eV upon cobalt encapsulation. The region in which these peaks are located is characteristic of elemental cobalt [74]. T. Fukumaru et al.’s work is an expansion on work conducted by

L-J Li et al. who laid the groundwork, showing the method to be successful and T. Fukumaru et al. examined its applications in n-type doping and thermoelectrics [12, 13].

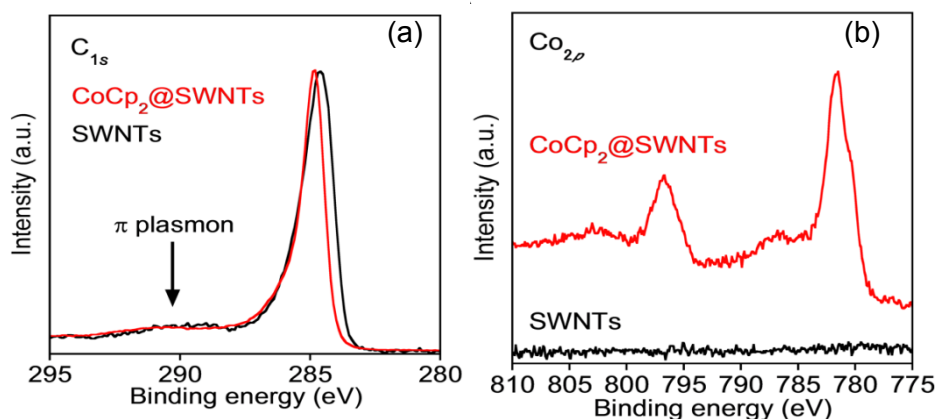


Figure 10: (a) XPS narrow scans of (a) Cobalt and (b) Carbon for cobaltocene encapsulated (red) and 'pristine' (black) SWCNTs. Reproduced from [12] Copyright (2015), with permission from Nature Publishing Group.

Unfortunately, although encapsulating the dopant within the nanotube is an elegant solution to insulate the dopant and provide air stability, it is achieved through a very specific method and one that would be difficult to reproduce and scale-up outside of a laboratory setting. Initially, SWCNTs are oxidised in air for 30 min and a further ten minutes at 360°C and 375°C respectively. The SWCNTs are then mixed with an excess of cobaltocene in a quartz tube under a nitrogen atmosphere at a pressure of 10^{-3} torr, heated to 100°C and left under these conditions for three days [13]. The cobaltocene-SWCNTs are then dispersed in a 1:1 mixture of toluene and methanol before being filtered and washed in toluene and methanol.

This being said the thermoelectric properties of the cobaltocene-SWCNTs were impressive as demonstrated within this work. T. Fukumaru et al. focussed on electrical conductivity, Seebeck coefficient and power factor [12]. Improvements were seen in each of these factors on encapsulation of cobalt where the electrical conductivity increased by a factor of ten likely due to the addition of the cobalt metal. The Seebeck Coefficient was seen to 'change sign' in that it transitioned from $50\mu\text{V}\cdot\text{K}^{-1}$ to $-50\mu\text{V}\cdot\text{K}^{-1}$ on encapsulation and the power factor, being the amount of power generated by the thermoelectric system at a particular temperature, was seen to jump drastically on encapsulation of cobaltocene and then increase gradually with temperature. This data is illustrated in Figure 11.

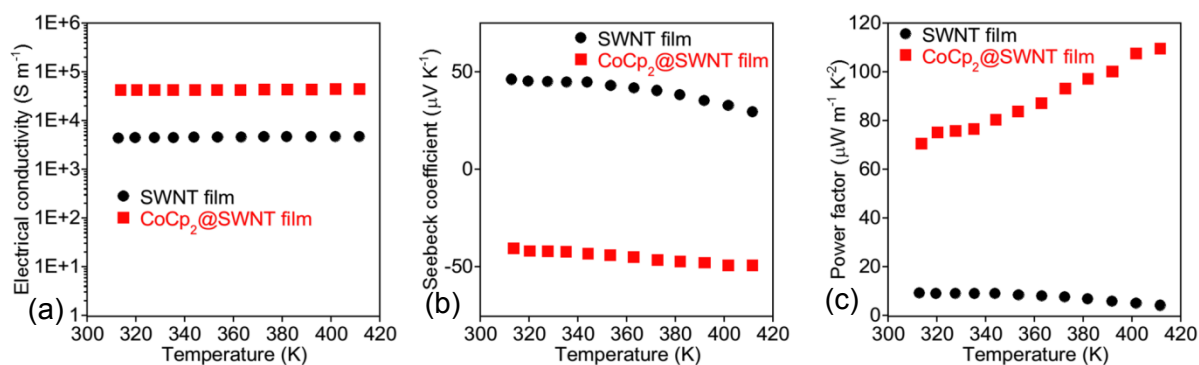


Figure 11: (a) Electrical Conductivity (b) Seebeck coefficient and (c) Power factor of Cobaltocene encapsulated (red) and 'pristine' (black) SWCNT films. Reproduced from [12] Copyright (2015), with permission from Nature Publishing Group.

4. Applications of n-type SWCNTs

The ability to use SWCNTs as n-type semiconductors is a great advantage as it allows fully organic electronic devices to be manufactured when combined with p-type SWCNTs or other organic p-type semiconductors. N-type SWCNTs have been used within many fields ranging from manufacturing transistors [11, 75-81] and thermoelectric devices [10, 12, 14, 15, 26, 64, 82-84] to chemical reactions [36-38, 43, 44, 85-89].

4.1. Transistors

Transistors are a pivotal component of modern electronics and are incorporated into every form of electronic device. Transistors are used for two purposes within electronics: amplification and current switching. Whatever the purpose of the transistor, semiconducting components are required. Today, electronics form a fundamental part of every day from driving to work to an evening coffee and therefore transistors are in use everywhere. With this in mind, SWCNTs have been widely looked at as a replacement to semiconductors such as silicon due to their ballistic electrical transport, sustained electrical properties and chemical inertness [90]. Due to n-type semiconductors being a necessary part of any transistor, n-type doped SWCNTs have been looked at for transistor applications over recent years.

Some research has aimed to tune the threshold voltage of n-type doped SWCNT transistors [75]. Tuning the threshold voltage is an important ability in digital electronics as if it is not controlled the resulting circuit could be unreliable due to a high amount of electrical noise present within the system [75]. To tackle this problem H. Wang et al. set out to provide a scalable method of tuning the n-type nanotube threshold voltage. They achieved this through doping with dimethyl-dihydro-benzoimidazoles (DMBIs) and tuned the threshold voltage by varying the dopant concentration and the film thickness [75].

Differences caused by deposition method were also studied with vacuum and solution deposition methods tested.

The SWCNTs were first sorted into a purely semiconducting sample, separation was achieved by a method previously reported by the group [91]. Silicon substrates were then left immersed in a semiconducting SWCNT dispersion for 8 hours. Doping of these nanotube films was achieved by evaporating dopant onto the nanotube film or by spin coating the nanotube films with a dopant solution. The evaporation process controls doping through the film thickness while the spin coating doping process controls doping through the solution's dopant concentration [75].

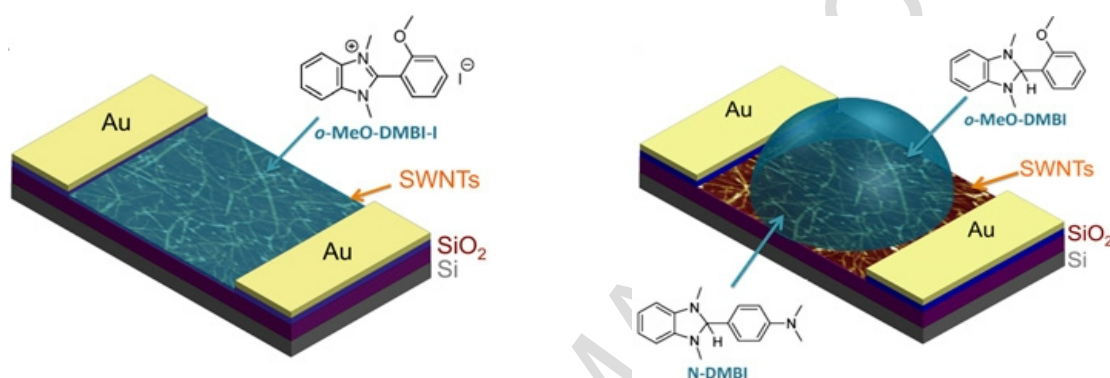


Figure 12: Schematics of n-type doping for thin film transistors prepared by (a) vacuum evaporation of *o*-MeO-DMBI and (b) solution processing of *o*-MeO-DMBI or N-DMBI. Reproduced from [75] Copyright (2014) National Academy of Sciences.

Each of these doping processes was successful in supplying the expected n-type semiconducting behaviour, where in both cases a shift towards semiconducting behaviour is observed. This is most clearly seen by the shift to a negative threshold voltage upon doping [75]. In both cases however there is a plateau in the n-type threshold voltages. This is attributed to a reduction in the electron mobility at higher film thicknesses [75]. This data serves to show there is no adverse effect to using solution processing over vacuum evaporation, or vice versa, for doping. In addition to the doping methods, two DMBI dopants, namely *o*-MeO-DMBI and N-DMBI, were tested for their n-type doping capabilities [75]. Solution processing was used to establish the n-type doping quality of these two dopants and it was found that N-DMBI provided a consistently 'higher negative' threshold voltage with increasing concentration indicating it was the better n-type dopant of the two. In transistors the on/off current ratio is an important consideration as this defines how easily the transistor may be switched on or off, a fundamental capability of transistors. It was observed that although N-DMBI provided a strong n-type

doping effect on the SWCNTs, it was perhaps too great as it was reported the ‘off’ current of the transistors after doping with N-DMBI was much larger than previously [75]. Such a result indicates the potential for instability in the transistors switching ability meaning it may be unsuitable for use in digital circuits [75].

One method of n-type doping that lends itself nicely to the field of transistors is in encapsulation. This is not encapsulation of a material within the SWCNTs as was discussed earlier [12, 13] but rather this method refers to encapsulating the nanotubes themselves within a thin film of dopant [91, 92]. With this encapsulation one may presume an electron transfer mechanism, where a dopant will donate electrons to the nanotube thus reducing it and inducing n-type behaviour but there is a second mechanism that has been shown to be quite useful, Field-effect doping [77]. Simply put field-effect doping is doping by contact rather than encapsulation where one will ‘stack the deck’ with positive charge carriers on one side of the intended n-type semiconducting material [77, 93, 94]. The addition of these positive charge carriers in such close proximity to the nanotubes causes a change in the energy band forcing it to ‘bend’ downwards thus shifting the transfer characteristics to negative gate voltages [93] as illustrated in Figure 13.

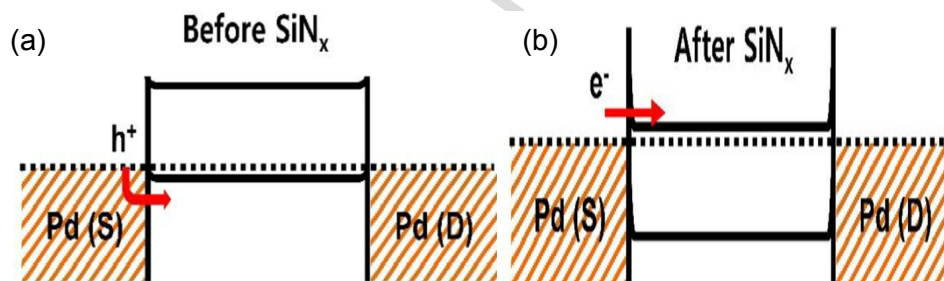


Figure 13: Qualitative band gaps of nanotube transistor in the ON-state (a) before and (b) after SiN_x , Field-effect doping. Showing the downward energy band bending due to doping. Reproduced from [77] Copyright (2015), with permission from the American Chemical Society.

This method has been attempted for transistors by various research groups in recent years, each using a different dopant to achieve their goals. The dopants used include plasma-deposited Si^+N_3 and metal oxides such as hafnium oxide (HfO) and aluminium oxide (Al_2O_3) deposited through atomic layer desorption [93]. Conveniently, this method of doping also insulates the nanotubes preventing air from impacting on the doping. This leads to a highly air stable system with a longer lifetime than other doping methods.

One such case of Field-effect doping SWCNTs was published in 2015 by T-J. Ha et al. [77] The method presented doped SWCNTs with plasma deposited Si^+N_3 thin films to achieve n-type semiconducting behaviour. Si^+N_3 was chosen as it is known to contain fixed positive charges with a high density. These two properties mean Si^+N_3 would provide a high level of doping at the SWCNT surface [77]. Devices were manufactured through firstly cleaning a SiO_2 substrate with acetone, methanol and isopropanol before being treated with an oxygen plasma. Poly-L-lysine was then drop-cast on the SiO_2 to facilitate the surface functionalisation needed for SWCNT deposition. After nanotube deposition, photolithography and electron-beam evaporation were used to pattern the source and drain contacts followed by patterning of the SWCNT network using photolithography and O_2 plasma etching [77]. The results show that doping by this method is effective and air stable with n-type behaviour persisting through a 30 day exposure to air. Indeed the results show very little change in nanotube behaviour indicating that the n-type doping may still be effective after more than 30 days [77].

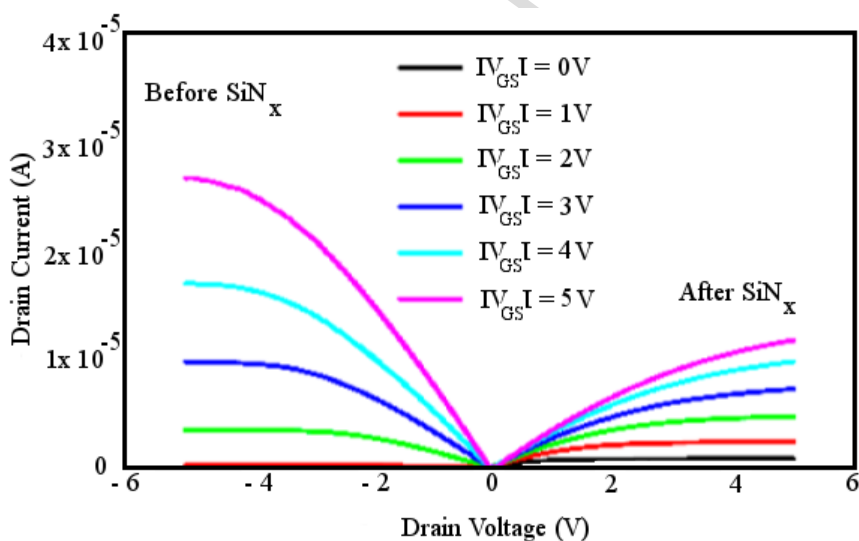


Figure 14: output characteristics of a SWCNT thin-film transistor before (left) and after (right) SiN_x doping. Reproduced from [77] Copyright (2015), with permission from the American Chemical Society.

The electrical properties of transistors manufactured using T-J. Ha et al.'s n-type SWCNTs are also desirable. Measurement of the drain current at various gate and drain voltages showed a linear increase in drain current with drain voltage indicating efficient injection of electrons at the source contact [77] (Fig. 14). Couple this with the fact that the doping level is such that gate modulation of the conductance is still a possibility and it can be said that high performance n-type thin-film transistors (TFTs) are possible from this method [77]. As well as the high air stability and good electrical properties, it was

observed that the choice of metal contacts makes no difference to the success of n-type doping by the Si^+N_3 . The major differences in changing metal contacts is in the ON-state current densities, where palladium was found to possess the highest [77].

T-J. Ha et al. [77] also manufactured a complementary metal-oxide semiconductor circuit through combining a p-type SWCNT TFT with an n-type SWCNT TFT doped with Si^+N_3 as discussed previously. This device was shown to be successfully operable and acts as a proof of concept for future devices manufactured in this way [77].

4.2. Thermoelectric materials

It is easy to see why thermoelectric devices and materials have received so much continued interest as generating electricity from simple heat is an exciting prospect that would be applicable to many industries and applications. As such, these devices and materials have received continued research interest and investment over the years.

Modern thermoelectric devices use semiconducting materials as the connections between the hot and cold sides of the circuit as is described in the figure 15 [95].

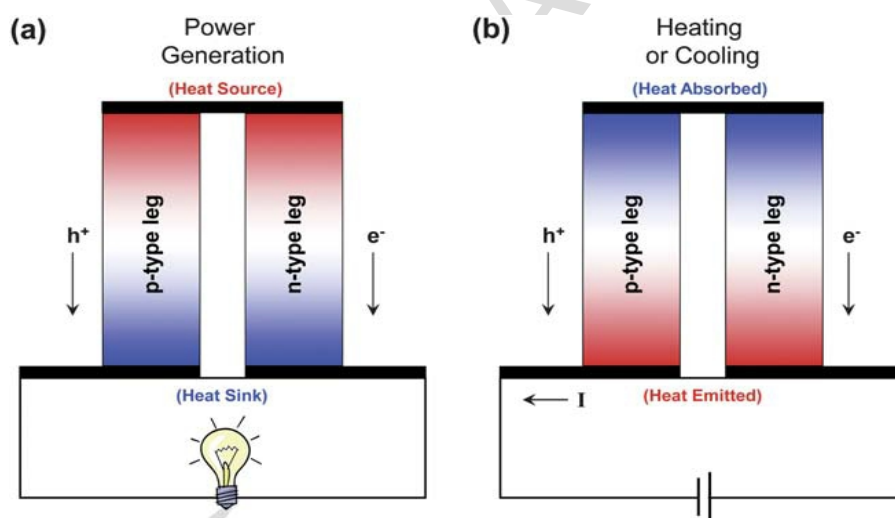


Figure 15: Schematic of thermoelectric devices used for (a) power generation and (b) heating and cooling.

Reproduced from [95] Copyright (2010), with permission from the Royal Society of Chemistry.

As has happened with many devices since the rise of nanomaterials, there has been a great effort to improve the performance of thermoelectric devices through the applications of various nanomaterials. The sheer wealth of information published on using nanomaterials in thermoelectric electric devices has prompted the writing of many review articles on the subject [95-106]. Due to their semiconducting abilities SWCNTs are seen as promising prospects for cheap, hardy and flexible thermoelectric materials. As a result of being able

to tune their semiconducting behaviour complementary thermoelectric devices consisting of both p- and n-type nanotubes have been developed [10, 26, 82]. However the majority of work into n-type doping SWCNTs in reference to thermoelectrics is into the effect doping has on the thermoelectric properties of the SWCNTs rather than manufacturing full devices.

Other work in this space puts forward a unique method of doping SWCNTs to be either p-type or n-type. This work applies conjugated polyelectrolytes (CPEs) with variable ionic functionalities to produce both p- and n-type SWCNT composites for flexible thermoelectric materials [82]. Varying the ionic functionality of the CPEs allows addition of extra positive or negative charge carriers thus doping the SWCNTs to be n-type or p-type. The structures of the electrolytes used by Mai et al. are shown in Figure 16 [82]:

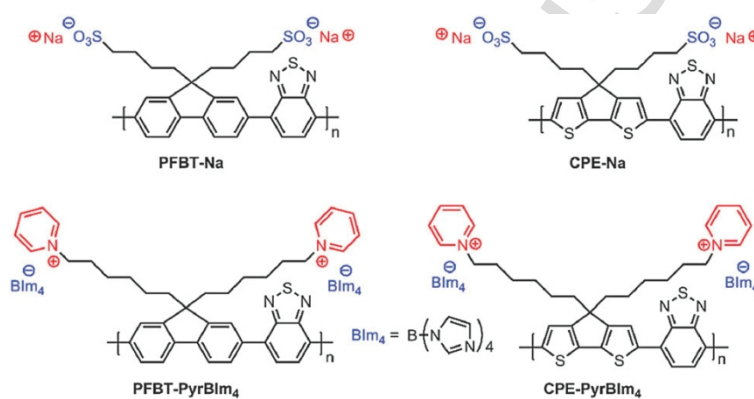


Figure 16: Chemical Structures of studied CPEs. Reproduced from [82] Copyright (2015), with permission from the Royal Society of Chemistry.

Measurements of the Seebeck coefficient at varying weight ratios of PFBT-Na:SWCNTs and CPE-Na:SWCNTs, respectively, show consistently positive values indicating constant p-type behaviour from both dopants. This p-type behaviour is likely provided by the SWCNTs in the mixture indicating no measureable doping provided by the PFBT-Na or CPE-Na ‘dopants’. However, addition of these ‘dopants’ to the SWCNT systems did cause drastic changes to the electrical conductivity and power factors of the thermoelectric materials manufactured in this process. Significantly higher electrical conductivities and power factors were observed for CPE-Na doped SWCNTs relative to the PFBT-Na doped SWCNT systems. This occurrence, although not directly discussed by the researchers, is likely due to differing backbone structures between the two polymers as their ionic functionalities are the same. Mai et al. do mention however that CPE-Na itself is p-type doped in solution and this may reduce the inter-SWCNT contact

resistance in the system leading to higher electrical conductivity [82]. If this is the case, the difference in conductivity and power factor likely has a much simpler explanation. Prior work by Mai et al. [107] supports the theory of CPE-Na 'self-doping' in solution, an ability PBFT-Na does not possess. This self-doping would likely provide the CPE-Na polymer with enhanced conductivity relative to PBFT-Na thus granting a generally higher conductivity range for the CPE-Na/SWCNT system than for the PBFT-Na/SWCNT system. The data presented by Mai et al. shows the Seebeck coefficient being dominated by the SWCNTs. However the trend in increasing conductivity would also appear to be dictated by nanotube content with the polyelectrolytes simply augmenting the conductivity ranges.

This does not mean to say the use of polyelectrolytes in thermoelectric materials or SWCNT doping is not viable. In fact the n-type doping section of this work shows successful n-type doping by the polyelectrolytes. However, the polyelectrolytes may not be necessary for p-type doping and similar effects could be observed through using simpler, cheaper conducting polymers.

In terms of n-type doping of SWCNTs by CPEs, Mai et al. do show successful n-type doping by polyelectrolytes [82]. This was achieved through the use of the same polymeric backbones as used previously however the ionic functionalities have been changed such that they are now positively charged with negative counter ions. This change lead to negative Seebeck coefficients for systems wherein the SWCNTs were not the dominant material in terms of weight [82]. Indeed as before the CPE backbone provided better electrical properties for the thermoelectric material and was shown here to be the better n-type dopant providing negative Seebeck coefficients at both 2:1 and 1:1 weight ratios of CPE:SWCNT. Additionally, proof that CPE-PyrBlm₄ acts as an n-type dopant is provided through measurements of electrical conductivity and Seebeck coefficient at varying CPE-PyrBlm₄ concentrations where a progressively more negative Seebeck coefficient is obtained at higher concentrations. The conductivity is also seen to fall progressively at concentrations higher than 2mg.mL⁻¹.

It is possible the n-type doping caused by the change in ionic functionality is achieved through an electron transfer reaction initiated by the negative counter ion. N-type doping by an electron transfer reaction has been discussed previously [14, 15]. However the mechanism by which the CPEs in this work dope the SWCNTs is not discussed by Mai et

al. A similar doping mechanism to Y. Nonoguchi et al.'s work [15] may be at play where after undergoing an electron transfer reaction with the negative counter ion the positively charged CPE will adsorb to the nanotube thus insulating it and maintaining its n-type behaviour. Mai et al.'s work provides a novel method of n-type doping SWCNTs with good thermoelectric properties.

5. Summary, Gaps and Progression of Research

This review discusses specifically a collection of the most promising methods of n-type doping SWCNTs published within the last decade. They have been highlighted due to their simplicity of method, outstanding n-type stability and electrical properties. Each of these methods represents an important step in recognising SWCNTs potential within cheap and environmentally stable electronic devices such as transistors and thermoelectrics. This review represents the first in-depth report on the n-type doping of SWCNTs considering not only methods of doping but applications and analysis of these techniques also. While the applications of n-type SWCNTs are quite broad, there are areas in which they may be applied that have not yet been ventured into, or at the very least published.

As discussed, much of the research into n-type doping of SWCNTs has been in the context of thin-film transistors and thermoelectric materials under the banner of flexible electronics. The major gap in the research and application of n-type SWCNTs is in the photovoltaics area where much of the literature almost exclusively discusses the use of p-type SWCNTs with an n-type semiconductor, predominantly silicon, to manufacture the solar cells. In fact p-type SWCNT containing photovoltaic devices have been extensively studied in literature [108-118] while n-type SWCNTs photovoltaics have only just recently been discussed in literature [119]. This lack of research is likely due to the stability of the n-type doping in air and the longevity thereof. Therefore it is simply easier to use SWCNTs as the p-type semiconductor in the solar cell. However, with the advances in n-type doping and air stabilities of the various doping methods recently published, SWCNTs may be viable in the organic photovoltaics arena.

Of the n-type doping methods discussed those involving electron transfer reactions seem to provide the most air stable and elegant processes by which SWCNTs may be n-type doped. Where, in most cases the electron transfer will reduce and thereby n-type dope the SWCNTs while the remaining now cationic 'n-type dopant' will be drawn to the SWCNT

and insulate it providing significant air stability as demonstrated by Y. Nonoguchi et al. by salt-coordination [14] and organic nanoparticle doping [15]. The simplicity of these methods is their strength where if reproducible they may be easily implemented into the solar cell manufacturing process through a simple immersion process. Alternatively, attempts could be made to modify these methods to allow solution doping to take place whereby SWCNTs would be doped prior to film deposition while they still sit in dispersion.

The semiconducting behaviour of SWCNTs remains something many researchers aim to control with n-type doping methods represent only one doping type. P-type doping methods have also been discussed in literature for SWCNTs however these methods lie outside of the scope of this review. While ‘intra-molecular’ doping is another interesting prospect currently being investigated that can provide intrinsic, p- and n-type semiconducting behaviours along a single SWCNT. This technique has applications within photovoltaics and transistors [119, 120].

Additionally, many publications specify doping methods where bucky papers or pre-deposited films are being doped. However, there are few methods by which SWCNTs are n-type doped prior to film deposition i.e. dispersion based doping methods. Such a doping process would arguably be much simpler than doping a pre-deposited film as the consideration of the dopant’s effect on the substrate or overall device may be removed as the film could be deposited as a simple manufacturing step with no extra work required. This is likely part of the reason PEI doping has been popular as it may be done in solution, could the air stability issue be solved it would likely be one of the standout doping processes.

For n-type SWCNTs to move forward as electronic materials there must be an effort to scale-up the device to useable sizes. While the research discussed within this review provides elegant, simple methods for n-type of SWCNTs with good electrical properties each of the measurements was collected on the laboratory scale. There needs now to be studies conducted within these areas to create devices, fully organic or hybrid, that satisfy the sizes required for commercial production to show these n-type SWCNT materials can be incorporated in the bigger picture and have manufacturing procedures put in place accordingly. The flexible electronics applications of the n-type SWCNT should lend themselves nicely to such a study.

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