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Interconnecting Carbon Nanotubes for a Sustainable Economy

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<http://dx.doi.org/10.5772/51781>

1. Introduction

Concerns about depleting natural resources have been circulating for decades with alarming predictions that have turned out to be less than accurate. What has become clear, however, is the need for a decrease in the utility of a fossil based economy and a focus on a more sustainable one. This chapter reviews some of the recent progress made in the use of interconnected carbon nanotubes (CNTs) in the hydrogen, photovoltaics and thermoelectric alternative energy based economies.

The move towards a hydrogen economy is a concept that has gained traction over the last 5 years with advances in hydrogen fuel cells that are economically viable. It is envisaged that the automotive industry will begin to implement measures for the development of vehicles with hydrogen fuel cells as the economy begins to recover. However, such a move will also require a substantial investment in the infrastructure to support these vehicles. Key to the development of such technologies is the need to continuously improve the efficiency, while monitoring the safety. CNTs have been used as frameworks for a number of key areas in the hydrogen economy [1]. The most notable area is that of fuel cell integration, where the tubes are mixed with platinum or palladium to aid in the process of catalysis.

CNTs with palladium attached to their surface have also been used for the construction of hydrogen sensors, expanding the research field from the consumption to the detection of hydrogen. The recent advances in cross-linked CNT papers are stimulating the development of new materials, such as flexible palladium embedded CNT sensors [2] (Fig. 1.). This section of the chapter will explore some of the latest results from the use of interconnected CNTs in hydrogen fuel cells and sensor development.

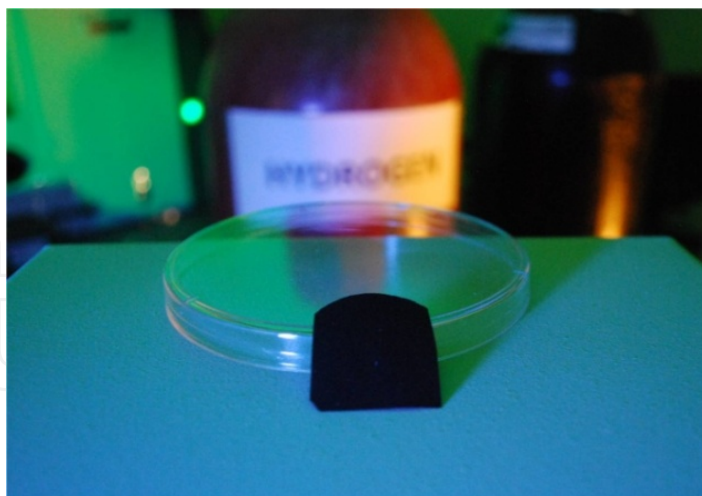


Figure 1. A cross-linked CNT paper with embedded Pd nanoparticles that can be used to construct a hydrogen sensor.

The field of photovoltaics is regarded as a major contributor to a sustainable economy. However; purveyors of large scale solar panels have been experiencing a degree of volatility in the market due in part to the decreasing price of the technology, increased competition and a dependence on government subsidies. At the opposite end of the scale, there is a surge in small solar powered gadgets such as pocket LED torches and mobile device chargers, which adorn many airport convenience outlets. The demand for pocket sized solar powered devices is helping to stimulate research into making the energy conversion process more efficient. There were three major advances in photovoltaics, the development of photovoltaic devices from crystalline silicon, which dominate the commercial market, cadmium telluride (CdTe) and dye sensitized solar cells (DSSCs). CNTs are currently being investigated as a way to enhance electron transfer and replace the standard platinum based counter electrodes, especially with DSSCs. CNT thin films and mats are currently being tested as components of these photovoltaic devices. This section of the chapter will explore how the CNTs have been used to enhance dye-sensitized [3], CdTe [4] and silicon [5] based solar cells, and address some the concerns about the race to produce novel photovoltaic devices and the toxic warnings from the past that may ultimately define the balance between safety and efficiency.

The last section of this chapter will focus on the development of CNT based thermoelectric devices which may bridge the gap between conventional and sustainable economies. Energy loss in the form of heat is clearly an important concept to address, and capturing the heat from combustion engines is one avenue being pursued by research. Around 75% of the energy produced from fuel with internal combustion engines is lost to the environment, so it may be possible to recapture some of this energy using a thermoelectric device between the engine coolant system to the exhaust manifold [6]. However, problems have been encountered with low efficiency so CNTs have been investigated as a suitable component of thermoelectric devices due to a number of characteristics, such as their low dimensional structure, their electrical conductivity, and their axial thermal conductivity [7, 8].

2. The Hydrogen Economy

Many nations are looking into alternative sources of energy to address issues of environmental responsibility and energy independence. Some of these energy sources include solar power, wind energy, natural gas, and hydrogen. As society explores hydrogen as an alternative energy source, the question is how effective can CNTs be in helping to solve some of the problems in the structure, function and safety of this emerging industry?

2.1. Fuel Cells & Hydrogen Storage

In the simplest case, a hydrogen fuel cell is comprised of a permeable membrane placed between an anode and a cathode. There are various types of fuel cells: polymer electrolyte membrane, direct methanol, alkaline, phosphoric acid, molten carbonate, and solid oxide. Hydrogen fuel cells fall under the polymer electrolyte membrane fuel cell (PEMFC) category and are sometimes also referred to as a proton exchange membrane fuel cell. In a typical PEMFC, the permeable membrane consists of a proton-conductive polymer such as perfluorosulphonic acid, also known commercially as Nafion. The fuel cell works by using a catalyst to oxidize hydrogen at the anode, converting it into a positively charged proton and a negatively charged electron. The electrons travel through a wire creating an electrical current to power a device while the protons travel through the permeable membrane to the cathode. At the cathode, the protons recombine with the electrons and react with oxygen to form water which is eventually drained from the system.

Despite recent advances in research, there are still a few obstacles that need to be overcome in order for fuel cells to become mainstream technology. In order to integrate with existing technologies, fuel cells need to become considerably cheaper. Currently, they are expensive to construct, mainly due to the use of platinum catalysts. According to the United States Department of Energy, the cost per kilowatt would need to decrease in order for fuel cells to be competitive and economically viable. In order to compete commercially with the combustion engine, it is estimated that the fuel cell cost would need to be cut to approximately \$25–\$35/kW. Another aspect of fuel cells that needs improvement is the operational lifetime. The permeable membrane is made of a synthetic polymer which is susceptible to chemical degradation. Reliability in automotive applications, can be defined by the lifetime of a car engine, approximately 150,000 miles, so research has focused both on improving the efficiency of the catalytic process and the durability of the components. CNTs have been proposed as a substitute to the carbon powder currently used in PEMFCs. (Fig. 2.) CNTs have excellent conductive properties, a low mass density, and robust physical properties making them an ideal and durable material for fuel cell electrodes. Furthermore, nanotubes assembled into such macrostructures have a high surface area making them a suitable substrate for Pt catalysts and hydrogen adsorption [9].

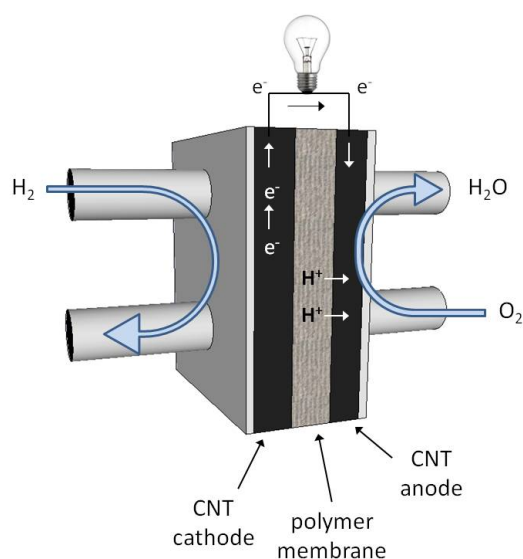


Figure 2. Schematic of a CNT composite hydrogen fuel cell.

In 2003, researchers from the University of California, Riverside explored the use of MWCNTs as a carbon support for platinum catalysts in an attempt to maximize Pt interfacing between all the components in a fuel cell. The problem in conventional fuel cells is that the addition of the polymer tends to isolate the carbon particles reducing electron transport, resulting in the requirement of additional Pt particles to increase the power output. To resolve this issue and improve conductivity, Wang et al. grew nanotubes directly on carbon paper and electrodeposited Pt particles onto the CNTs [10]. Although their experiments produced promising results, their CNT based fuel cell still had a lower performance compared to conventional PEMFCs. Despite this low performance, this proof of concept was important to other researchers using CNTs in fuel cells. The following year in 2004, Girishkumar et al. investigated ways to improve the electrodes in direct methanol fuel cells (DMFCs) [11]. Their team developed a way to synthesize SWCNT thin films onto optically transparent electrodes using electrophoretic deposition techniques. It was determined that there was an improvement in catalytic activity mainly due to a larger surface area provided by the CNTs. This high surface area and porosity maximizes interactions between the fuel, electrode, and catalyst interface thereby enhancing Pt utilization and potentially reducing fuel cell manufacturing costs. Li et al. (2006) also explored the use of CNTs in PEMFCs. They developed a facile and cost-effective method for the synthesis of an aligned Pt/CNT film [12]. They were interested in producing oriented CNT films due to enhanced conductivity. It was also suggested that there would be higher gas permeability and better water removal with aligned nanotubes. The aligned CNTs did show an improvement in Pt utilization as 60% of the metal particles were being used during catalysis [11].

Using covalently cross-linked CNTs is another promising avenue for fuel cell electrodes [13]. Our work at Florida State University focused on the covalent cross-linking of multi-walled carbon nanotubes via a Michael addition reaction mechanism to form thin, flexible mats

[14]. We then explored an alternative cross-linking system to avoid the use of thiols and embedded palladium nanocrystals into the cross-linked network [2].

Research into hydrogen storage with interconnected CNT networks started by looking into SWCNTs using a procedure called temperature programmed desorption. Experiments on MWCNTs followed with work focusing on metal doped tubes. However, problems began to arise when increasing values of CNT storage capacities, up to 21 wt%, were reported. A detailed review of the findings can be found by Yunjin Yao and serves as an interesting footnote towards the role of CNTs and the need for a better understanding of their chemistry in materials [15]. In summary, the main concerns were that elevated hydrogen storage percentages may have been due to a number of factors including the insufficient characterization of CNT composites due to the presence of SWCNTs, DWCNTs and MWCNTs with a variety of open and closed ended tubes. Contamination of the CNTs during the process of ultrasonic probe treatments was a concern, because in one example the value for SWCNTs were reported to have a hydrogen storage capacity of around 4.5% at 30 kPa and 70 K, but the ultrasonic probe was made from a titanium alloy that was known to act as a hydrogen storage material.

2.2. Water Splitting

The research field based on water splitting has, not surprisingly, found a niche in the development of the hydrogen economy due to the clean production of hydrogen and oxygen. However this integration has a far more significant impact when combined with hydrogen fuel cells. The waste product of hydrogen fuel cells is water, and it is formed during the reaction with oxygen, so the water could fuel the process of splitting and this in turn can fuel hydrogen cells.

CNTs have been used to enhance the water splitting performance of titania photocatalysts [16] but an alternative use for CNTs has been found in membranes. Nafion, a sulfonated tetrafluoroethylene based fluoropolymer-copolymer, is a membrane that has had commercial success in the fuel cell industry. Research groups are looking into enhancing the properties of the film with the addition of CNTs. Nafion/CNT composites with low concentrations of CNTs have been shown to have an effect on solvent permeation and mechanical stability. At high concentrations of CNTs the membranes have the ability to separate proton and electron conduction pathways in the membrane. Using this concept, many applications can be envisaged for these membranes with one example being that of using sunlight to produce hydrogen from water splitting. Current research has focused on the measurements of the electron and proton transport characteristics of Nafion and MWCNT composite films.[17] These films can be assembled by the addition of Nafion solution to MWCNTs, followed by the dispersion of the MWCNTs in an ultrasonic bath. Various concentrations of MWCNTs were investigated to a maximum of 5% MWCNTs by dry weight of Nafion. After the addition of isopropyl alcohol, to further aid the dispersion of the MWCNTs, the slurry was poured into petri-dishes and left to undergo solvent evaporation for 3 hours. The dishes with various

CNT concentrations were placed in an oven set to 40 °C for a few hours before being washed with deionized water and removed from the petri-dishes.

To test the membrane, an artificial leaf system was constructed. (Fig. 3.). The membrane separated the anode, which was exposed to sunlight where water droplets were present, and the cathode.

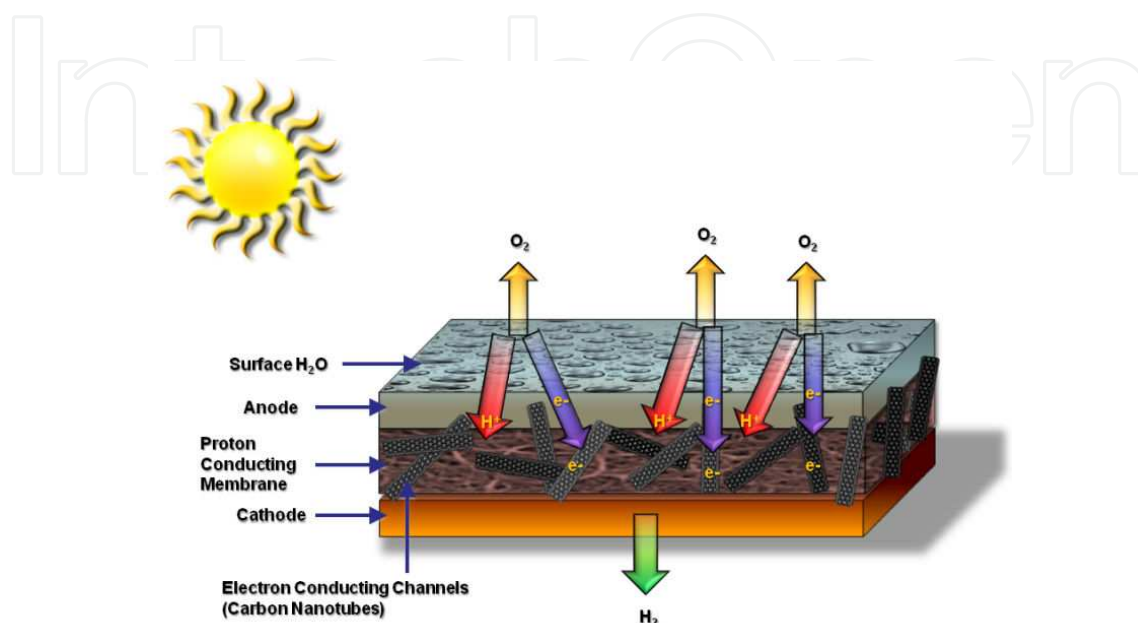


Figure 3. Schematic of the water-splitting device. The anode contained a chromophore and an oxygen evolving complex. The cathode contained a proton reducing catalyst. Image adapted from V. Ijori *et al.* (2010).

The results highlighted a few points. Firstly pure Nafion exhibited insulating behavior and with increasing MWCNT percentage, a non linear behavior is observed with I–V curves, which is an indication of non-ohmic conductivity. The membranes were tested in both wet (1% H_2SO_4) and dry conditions to evaluate the electron conductivity. Before and after wetting the conductivity values increase with increasing filler content, but again without a linear relationship, which meant a critical concentration at which the membrane changed from insulating to conducting/semiconducting had to be established. This was done by looking at the values higher than 10^{-1} mS/cm which were obtained when MWCNTs > 3%. The next task was to investigate proton conductivity, and with standard conditions, this was generally low. However, with an increasing MWCNT percentage there was a subsequent increase. Although the effects of MWCNTs on proton conductivity is still not fully understood, most researchers will fall back on the semi-empirical quantum mechanical calculations too at least provide an insight into the possible conduction pathways.

When the membranes were subjected to 1% H_2SO_4 they did show an increase in proton conductivity, which was due to the various proton transfer mechanisms. The hydrogen bonding of the $-\text{SO}_3$ groups with an H_3O^+ ion and water molecules results in a change in the side chains of Nafion. It was difficult to determine the contribution of MWCNTs in the

process of electron transfer because of the amount of water molecules. However membranes with no MWCNTs demonstrated the best proton conductivity, while the others have slightly lower conductivities. The answer could be as simple as a decrease in the amount of Nafion. Either way, this study has shown great potential for the integration of CNTs for membrane applications.

2.3. CNT Hydrogen Sensors

Another application of great interest in the field of CNTs is hydrogen sensing. Advancements in the development of fuel cell design and technology means that a variety of sensors would be required to maintain a safe operational environment. CNTs are an ideal material for components of sensors due to their durability, and electronic properties.

One of the first breakthroughs in CNT sensor technology occurred in 2001 when Kong et al. constructed hydrogen sensors by decorating SWCNTs with Pd nanoparticles [18]. Their H₂ sensor exhibited significant changes in conductivity when exposed to small amounts of H₂ and was able to operate at room temperature. Kong et al. were able to achieve this by depositing Pd particles on CVD grown SWCNTs via electron beam evaporation methods. When they placed this in a hydrogen atmosphere, a decrease in the CNT conductivity was observed. It has been proposed that this lower work function promotes electron transport from the Pd NPs into the CNTs resulting in a decreased amount of hole-carriers and conductivity. The reaction is also reversible. Under a hydrogen atmosphere, Pd reacts with H₂ to become palladium hydride. The dissolved hydrogen in Pd metal combines with oxygen in air and results in H₂O, recovering the electrical characteristics of the sensor. Kong et al. reported that their detector had a limit at 400 ppm, a response time of 5-10 s, and a recovery time of approximately 400 s [18].

One design principle of CNT composites that has defined the nature of efficiency is that of aligned CNTs. From aligned thin films of Buckypaper to forests of vertically grown CNTs on substrates, control over the direction of individual tubes and connected bundles is essential for unlocking the full potential of the tubes. An investigation was made into the development of aligned CNT sensors using a method involving nanoplating and firing to produce cracks in a CNT composite film, exposing horizontally aligned carbon nanotubes (HACNTs) [19]. This research used arc produced MWCNTs as the basis for the composite film, which was rather enlightening in a field geared towards chemical vapor deposition (CVD) produced tubes. Research with arc produced MWCNTs has almost become a relic of the early years of CNT research. They were made by using a 150 mm long graphite rod for the anode and a graphite disc on a copper block for the cathode. After purification steps the CNTs were acid-oxidized using the standard 3:1 ratio of nitric acid (HNO₃) to sulfuric acid (H₂SO₄) and washed several times in DI water before being dried in air at 120 °C. The acid treatment was required to increase the interfacial adhesion between the CNTs and metals. To produce the sensor, a sample of the purified CNTs was dispersed in DI water with a polyvinylpyrrolidone surfactant (PVP K30), which produced a CNT suspension. The CNT/Ni

composite was produced by the addition of nickel sulfate solution containing sodium phosphate, maleic acid disodium salt hydrate, citric acid monohydrate, lead(II) acetate trihydrate and sodium acetate trihydrate. The composite film was produced on a glass substrate by the immersion of the glass, with palladium particles on the surface, into the CNT/Ni solution for 60 seconds before drying the substrate at 100 °C to induce cracks in the film (Fig. 4.) exposing horizontally aligned CNTs. 18 Finger platinum electrodes were then deposited by DC sputtering to complete the sensor.

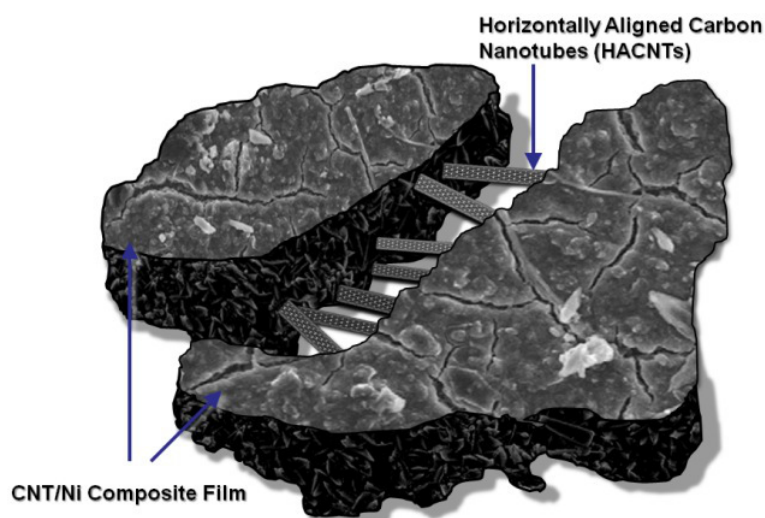


Figure 4. Schematic of the cracked composite film exposing horizontally aligned CNTs.

These results are described in two papers and although the idea of horizontal alignment is important, it is difficult to accurately quantify the results of the papers since in both cases there is an abundance of nanoparticle palladium in both the CNT/Ni system (Pd deposited on the glass) [19] and the Pd/CNT/Ni (Pd deposited on the CNT/Ni film) system [20]. Fig. 5. shows the process of assembly for the sensors, which use a similar procedure in both of the research papers.

The HACNT-based sensors were also shown to have a sensitivity response to carbon dioxide, methane and ethene with a gas concentration of 200 ppm, with the highest sensitivity for H₂. One of the points raised in this research, that was fundamental to the mechanism of sensing, was the role of atomized hydrogen. These atoms, produced by the metal particles, migrated to the sidewalls and the defects of CNTs, diffusing into the lattice of nanoparticles. It was stated that a dipole layer formed at that interface and affected the charge-carrier concentration, and the hydrogen atoms donated their electrons to the CNTs, which resulted in a decrease in conductivity.

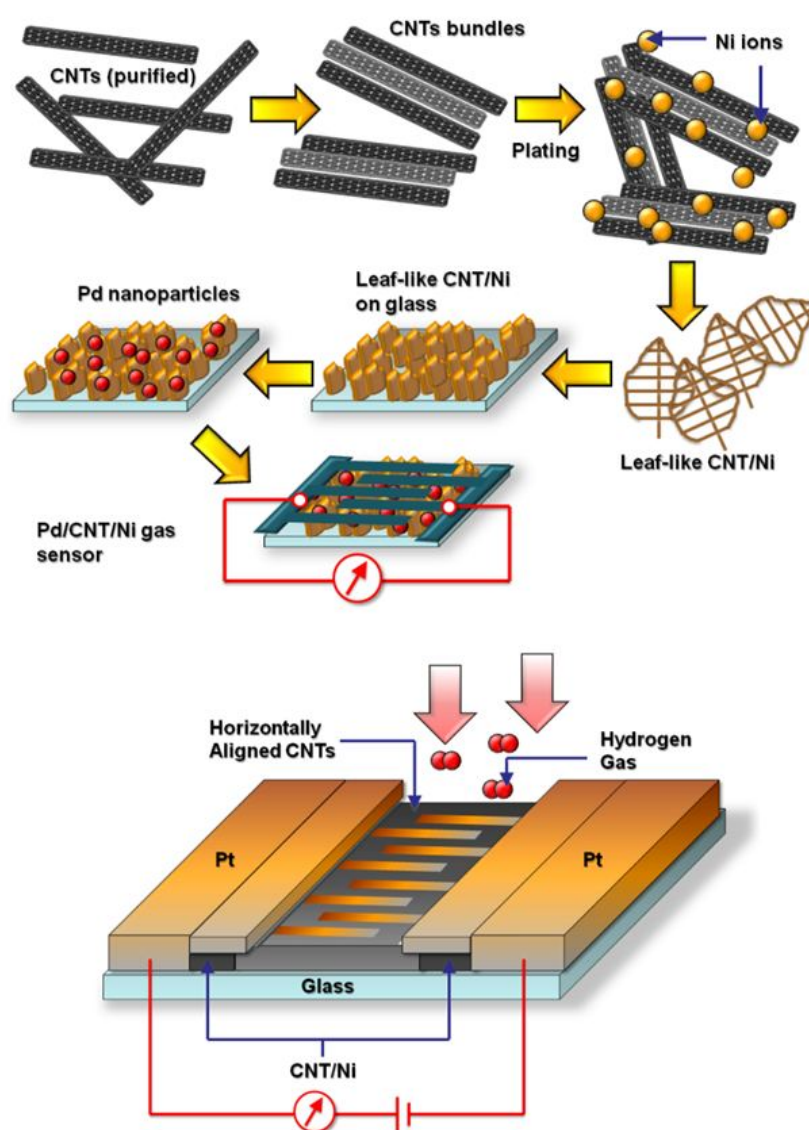


Figure 5. Schematic of the steps involved in the construction of hydrogen sensors on glass substrates with the use of the Pd nanoparticle functionalized CNT/Ni composite film. Image adapted from Lin *et al.* (2012). Schematic illustration of a HACNT-based gas sensor on glass substrate. Image adapted from B-R Huang *et al.* (2012).

In another example, a hydrogen sensor was constructed using SWCNTs and chitosan (CHIT).[21] The CHIT which covered the SWCNTs was able to filter out polar molecules and allow hydrogen to flow to the SWCNTs. The CHIT conjugate which is porous is insulating by nature, but can be made water soluble in an acidic environment which is then useful for making a film. Additional benefits can be found in the many functional hydroxyl ($-OH$) and amino ($-NH_2$) groups that react with analytes, so the effect Of a CHIT conjugate with SWCNTs for the development of a hydrogen sensor was investigated. The CHIT film was prepared by making a 2 wt% solution dissolving CHIT in a 5% acetic acid solution. This was used to coat a glass substrate or SWCNTs depending on the sensor preparation and followed by the removal of solvent to form the films. To evaluate the sensor performance three

different types were made (Fig. 6.). The Type I sensor was assembled simply by depositing SWCNTs onto the glass substrate with Pt electrodes placed by sputter deposition. The Type II sensor was assembled by casting the glass slide with a film of CHIT before being placed into an arc-discharge chamber to deposit SWCNTs. The Pt electrodes were added in a similar method. The Type III sensor was assembled using the initial preparation for a Type I sensor followed by CHIT film coating and Pt electrode deposition. There were slight differences in the interaction of the CHIT film with the SWCNTs. In the Type II sensor, there was some mixing of the CNTs with CHIT but only at the interface. With the Type III sensor, the CNTs were immersed in the CHIT matrix.

Resistance measurements of the films were made between the electrodes, and the values were around $100\ \Omega$ for Type I and II films and around $10^6\ \Omega$ for the Type III film. The high resistance could be accounted for by the contact of the electrode with chitosan, although it was noted by the authors that ohmic contacts were present.

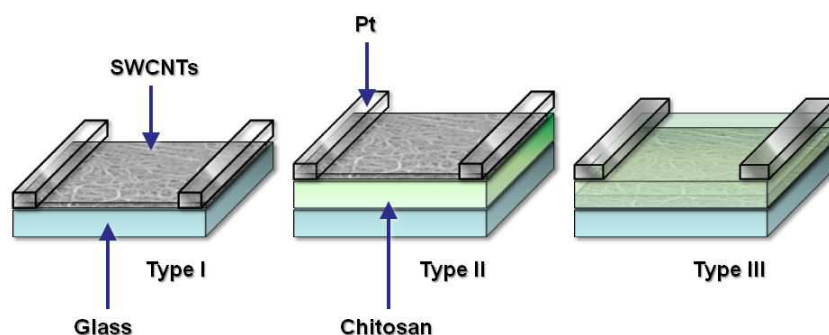


Figure 6. Diagram of the 3 types of sensors. Image adapted from Li *et al.* (2010).

The response of the sensors was measured at room temperature and the results showed 15, 33, and 520% for Type I, Type II, and Type III sensors, respectively. One interesting point made by the authors was that although the Pd decoration of SWCNTs is typically used to enhance hydrogen sensing, the response can be less than the effect of chitosan at 4% H_2 gas. This research provided an important step towards the use of CNTs in sensors without the requirement of Pd.

In summary, the use of CNTs in the hydrogen economy has highlighted some interesting points. Is the race to develop more efficient hydrogen powered devices really producing a sustainable economy? And has the focus on reducing the utility of some of the rare raw ma-

terials been lost? It is well known that platinum and palladium are extremely important to the fuel cell and sensor industries, with CNTs enhancing their properties, but an increase in alternative energy devices based on these metals, whatever the concentration, may cause issues of sustainability in the future.

3. Photovoltaics

The research field of photovoltaics has certainly become a hot topic over the last few years with a lot of attention based on increasing the efficiency of dye sensitized solar cells (DSSCs) in the hope that they will one day be as prevalent as the silicon based alternative. CNTs are an important addition to the field of photovoltaics with the focus on the nanotubes acting as p-type materials or enhancing/replacing the counter electrodes.

3.1. Dye Sensitized Solar Cells

If there were an enclave for truly beautiful chemistry, then the research behind dye sensitized solar cells (DSSCs) would clearly be the centerpiece. The chemistry behind the operation of these devices is inspiring a generation of researchers to address the concerns of renewable energy with a different approach to the well established silicon based solar cells. Generally, the DSSCs are comprised of an anode, electrolyte and cathode. The anode is usually assembled from nano-crystalline titania particles (TiO_2) and a dye attached to the particles. The cathode, also known as the counter electrode (CE), is where the catalysis must occur and typically contains platinum. The iodide electrolyte facilitates the iodide/triiodide redox couple where after the excitation of the dye and loss of an electron, it regains one from iodide, oxidizing it to triiodide. The best reported efficiency for DSSCs is 11.4% as documented by the National Institute for Material Science (NIMS).

CNTs have been used as a potential replacement for the platinum based CE. In a study by Jo et al. (2012), interconnected ordered mesoporous carbon-carbon nanotube nanocomposites were used to demonstrate Pt-like CE behavior in a dye-sensitized solar cell [22]. CNT fibers have been used as a conductive material to support the dye-impregnated TiO_2 particles. The CNTs were first spun from an array synthesized by chemical vapor deposition and resulted in highly aligned macroscopic fibers [23]. The research was novel in the application of these fibers as both the working electrode and the counter electrode.

The CNT/ TiO_2 composite fiber was produced by submersing the pure CNT fiber in a TiO_2 colloid solution which was followed by sintering at 500 °C for 60 min. The thickness of TiO_2 layer was determined to be between 4 and 30 μm , depending on the submersion time. The dye used for the cell was cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis (tetrabutylammonium) which is better known as N719. For DSSCs with a metal CE the I^-/I_3^- couple does eventually cause corrosion, but the CNT fibers exhibit a high stabil-

ity and are relatively cheap. Fig. 7. shows the schematic of the working device with the two fibers in an electrolytic solution.

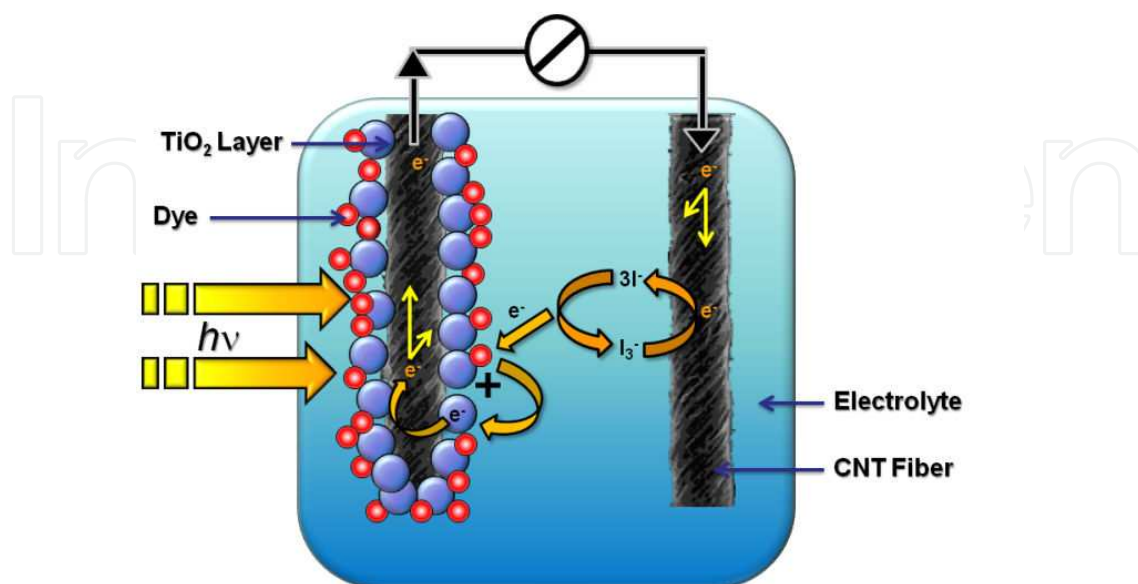


Figure 7. Schematic illustration of a wire-shaped DSSC made from two CNT fibers. Figure adapted from Chen *et al.* (2012).

The mechanical properties of the fiber are quite good with tensile strength measurements that exceed 700 MPa. The enhanced electrical conductivity also ranges from 100 to 1000 S/cm. The fiber-shaped DSSC demonstrated an efficiency of 2.94% which was a significant accomplishment. The fibrous nature of the material would make large-scale composites easy to fabricate. One of the more exciting applications is that of woven fabrics that may be used for the development of smart textiles for consumers, or extended use for space based electronics.

3.2. Quantum Dot Solar Cells

Cadmium telluride (CdTe) has been shown to be a promising low-cost component photovoltaic material, however the incorporation of quantum dot (QD) based technologies will likely raise fears about the toxicity of cadmium and cadmium based compounds. Significant progress has been made during the past several years with the highest efficiency reported for CdTe based photovoltaic devices at 17.3% produced by the company First Solar.

Although research is shifting towards CdTe/graphene composites [24], there is still room for CNT based devices. SWCNT/polyelectrolyte/QD nanohybrids have been produced that take advantage of the negatively charged thioglycolic acid capped CdTe QDs and SWCNTs coated with a positively charged polyelectrolyte facilitating electrostatic interactions [25]. In this

work, SWCNTs coated with a positively charged polyelectrolyte showed typical transitions and emission attributes in the visible and near-infrared spectrum. The application of steady state absorption spectra was useful in outlining the superimposition of QD and SWCNT characteristics. The results of the study also confirmed charge transfer between SWCNTs and QDs, underlined by femtosecond transient absorption spectroscopy. Microscopic studies suggested that statically formed SWCNT/polyelectrolyte/QD nanohybrids with individually immobilized QDs were generated. It is clear that this study focuses on the importance of the interactions between the components of the nanohybrids and creates a pathway for looking at the development of the layer-by-layer coating of SWNTs and recruitment of photoactive particles for photovoltaic applications.

3.3. Silicon Based Solar Cells

With the exception of multi-junction cells and gallium arsenide (GaAs) based devices, crystalline silicon based cells are still the best choice with efficiencies at 20.4% for multicrystalline structures to 27.6% for single crystal based cells. However, there is clearly room for improvement as the increase in efficiency has generally reached a plateau over the last few years. What may be required is a different approach to the design and chemistry of these photovoltaic devices. CNTs have again been applied on the strength of their p-type conduction. In one recent example, polyaniline (PANI) and CNTs were used to construct heterojunction diode devices on n-Type silicon [26]. It was found that both PANI and SWCNTs could act as photovoltaic materials in a bilayer configuration with n-type Silicon: n-Si/PANI and n-Si/SWCNT. Four devices were tested (Fig. 8.) and it was determined that the short circuit current density increased from 4.91 mA/cm² for n-Si/PANI (Fig. 8a) to 12.41 mA/cm² n-Si/PANI/SWCNT (Fig. 8c). The n-Si/SWCNT/PANI device (Fig. 8d) and its control n-Si/SWCNT (Fig. 8b) exhibited a decrease in the short-circuit current density.

PANI was synthesized using the MacDiarmid method [27] before being spin-coated at 600 rpm to form a film. The SWCNTs were dispersed in DMF by sonication over a period of 12 h in 3 hour intervals, with the any solids removed by centrifugation. The supernatant was then removed and sonicated for an additional 6 hours before being used to make the devices. The devices were assembled by spraying SWCNTs using an airbrush deposition technique at 150 °C. It was found that the characteristics of the devices were affected by their design structure with better hole transport from PANI to SWCNTs and less efficient transport of holes from PANI to SWCNTs in the multilayer devices.

Other examples of CNT-Silicon hybrid photovoltaic devices include the investigation of the optimal thickness of SWCNT films on n-type silicon in order to maximize photovoltaic conversion [28] giving percentage efficiencies between 0.4 and 2.4%, and the effect of the number of walls of MWCNTs on the photon to electron conversion [29].

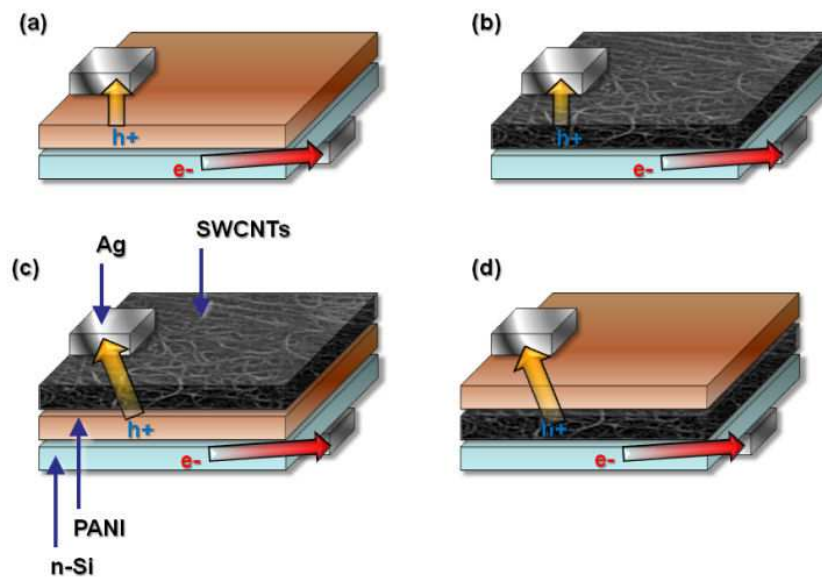


Figure 8. Schematics for (a) n-Si/PANI, (b) n-Si/SWCNTs, (c) n-Si/PANI/SWCNTs, and (d) n-Si/SWCNT/PANI devices. Image adapted from Bourdo *et al.* (2012).

In summary, photovoltaics have been shown to be very popular within the scientific field and the commercial market. Consumer electronics have been marketed with solar power chargers as a way to promote sustainability and environmental responsibility. The research into ruthenium based DSSCs is very popular but again there are concerns about the use of ruthenium for a sustainable economy. Fortunately, there are many photosensitive dyes that don't contain ruthenium which are currently being explored, but it is clear that the integration of interconnected CNTs can play an important role in the development of novel photovoltaic devices.

4. Thermoelectrics

In 1821 Thomas Johann Seebeck made the first discovery in the series of thermoelectric effects. The Seebeck effect described the electromotive force (emf) produced by heating the junction between two different metals. In essence, the kinetic energy of the electrons in the warmer part of a metal would facilitate the transfer of the electrons to the cooler metal faster than electron transfer from the cooler to the warmer metal, essentially creating an electronic potential where the cooler metal obtains a net negative charge. Harnessing the heat lost from a system and converting it to electricity will help to reduce the strain on electricity providers, but the difficulties surrounding the efficiency of the conversion process need to be addressed.

4.1. Thermoelectric Fabrics

One of the more futuristic ideas is that of wearable electronics, and this has been envisaged for many in the field of photovoltaics, but an interesting alternative can be found in the field of thermoelectrics. Recent advancements in research have shown that composite films of MWCNT and polyvinylidene fluoride (PVDF) assembled in a layered structure can be designed to have the effect of felt-like fabric.[30] A thermoelectric voltage can be generated by these fabrics as a result of the individual layers increasing the amount of power produced. More importantly, these fabrics would be more economical to produce clearing the way for a new generation of energy harvesting devices that could power portable electronics. Fig. 9. shows a schematic of a fabric with every alternate conduction layer made with p-type CNTs (B) followed by n-type CNTs (D). The insulating layers allow for alternating p/n junctions when all the layers are stacked, pressed and heated to melt the polymer. It was noted that layers A-D could be repeated to reach a desired number of conduction layers N , and when the film is exposed to a change in temperature ($\Delta T = T_h - T_c$), the charge carriers which can be holes (h) or electrons (e) migrate from T_h to T_c generating a thermoelectric current I .

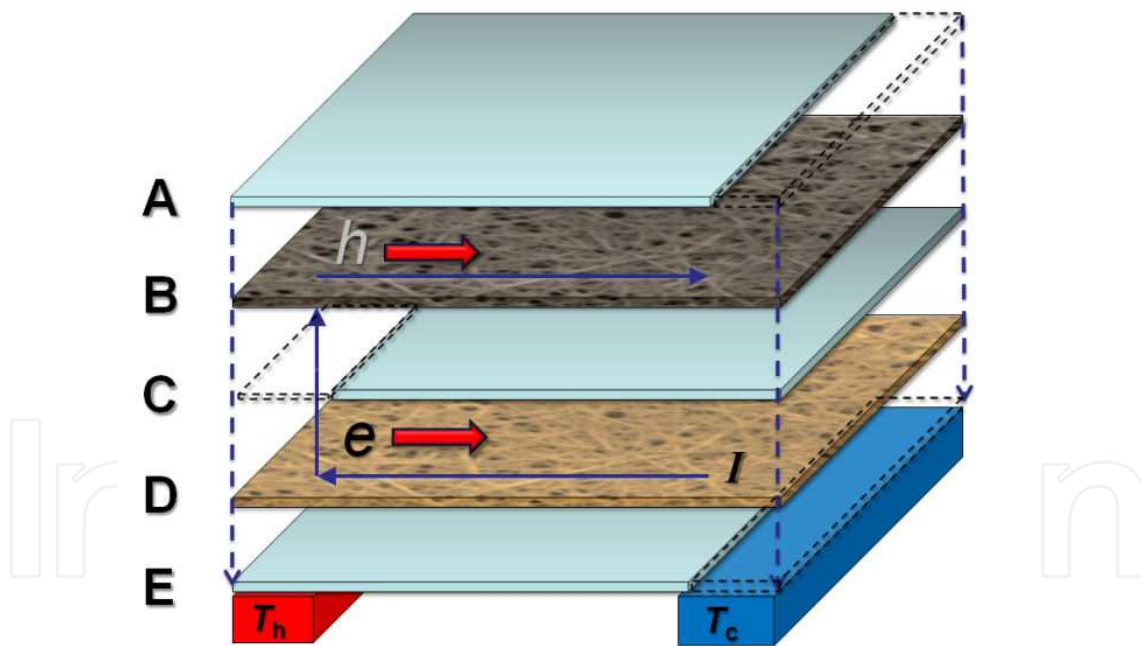


Figure 9. A Layered arrangement for the multilayered fabric. The CNT/PVDF conduction layers (B,D) are alternated between the PVDF insulation layers (A,C,E). Figure adapted from Hewitt *et al.* (2012).

When more power is required, ΔT would have to be increased. Subsequently, if the heat source were sufficiently large enough, the number of conduction layers could be increased. This would be a huge benefit for manufacturing industries that use high temperature equipment. In terms of energy output, a fabric composed of 300 layers with a $\Delta T = 100$ K, may

produce up to 5 μW . This is certainly a promising material that could potentially be integrated into many thermal systems and help with waste heat recovery.

4.2. Micro-Thermal Electrics

The addition of CNTs to microelectrical mechanical systems (MEMS) typically proceeds by either a bottom-up approach which focuses on the deposition of catalytic nanoparticles to control the location of CNT growth or a top-down which concerns the manipulation of the CNTs to the correct position. A top-down method was used to make a CNT thin film on a microelectrical mechanical system which was then characterized in terms of the thermoelectric coefficients of the aligned SWCNTs [8]. Using the process of 'super-growth' which incorporates water-assisted chemical vapor deposition, a CNT film was made and patterned by electron beam lithography into the required dimensions. By patterning a formed array of gold-SWCNT thermocouples it was found that under standard room temperature the Seebeck coefficient of the aligned SWCNT film was between 18 and 20 $\mu\text{V C}^{-1}$. The Seebeck effect of the SWCNT film was documented using thermocouples made of gold-SWCNT (Fig. 10.). Electrodes, a hot end and cold end temperature sensor, and a heater were produced by photolithography, and with a gold lift-off process on top of a silicon substrate that was covered by an insulating layer of Si_3N_4 . The SWCNT film was then constructed on the gold surface using the process of top-down assembly.

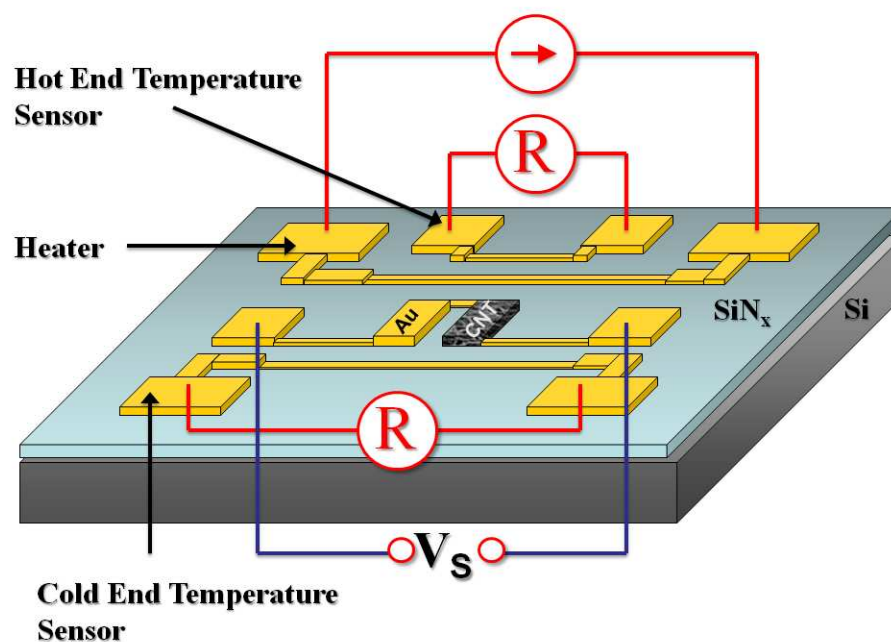


Figure 10. Schematic of a device for measuring the Seebeck effect in a CNT film. Figure Adapted from Dau *et al.* (2010).

When the device was used, an output voltage of 54 μV was recorded with a temperature difference of 3.07 $^{\circ}\text{C}$. This gave a Seebeck voltage of 19.38 $\mu\text{V K}^{-1}$ which on average re-

mained constant. Aligned CNT bundles may have smaller Seebeck coefficients (thermoelectric sensitivity) than randomly oriented CNTs. The authors suggested that the difference may be a result of the contribution of inter-tube barriers, relative to ΔT , although more work is required to fully understand the effect of CNT films for the integration of them into thermoelectric devices.

5. Conclusion

CNTs have seldom been just another material for novel composites, but their true potential has yet to be transferred from the nano- to macro-scale. More than a two decades after their discovery, their influence has reached almost every aspect of scientific research from engineering to medicine. Faced with concerns about sustainably and climate change, the use of CNTs have helped to transform our approach to renewable energy. Advances in hydrogen fuel cells with CNT composite electrodes or membranes are helping to reduce and eliminate the need for rare and expensive catalysts. Safety is also another issue for the hydrogen based economy. Many different types of sensors will be required to promote a safe operational environment especially when the ignition concentration of hydrogen can be as low as 4%. The same technology that is used in the catalysis process in hydrogen fuel cells can be used to create hydrogen sensors, and work with interconnected CNTs has provided sensitivity values that contend with conventional sensors.

The role of interconnected CNTs in the photovoltaic research field is popular because of the potential to make novel hybrid solar cells, whilst increasing the overall efficiency of the device. While the early results look promising, there are still some difficult questions to address, like how does the presence of defects on the CNT surface affect the chemistry and ultimately the efficiency of a DSSC?

The integration of CNTs into thermoelectric devices currently does not have the same level of development as the other alternative energy resources, possibly because the field is more geared towards cost saving on an industrial scale and the development of component systems for vehicles rather than consumer gadgets or devices, but research into waste heat recovery is substantial. It is likely that thermoelectric devices will conform more to a silent revolution with an uptake in industries that work with high temperature equipment looking at converting some of the heat produced back to electricity. However, the research into thermoelectric fabrics has shown the potential for consumer products that may find a market in the future.

In summary, we are beginning to see a shift towards alternative fuel sources, with a focus on hybrid technologies like those found in the automotive industries, but we need to address the impact of our current economy as we transition to a more sustainable one.

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