Unwritten potential: Changing the Face of Solar Energy with Carbon Nanotubes

By

Derek Repka

Science 100

April 2015

Introduction

One of the greatest challenges that face the world is finding a reliable and sustainable source of clean and renewable energy. Many different approaches have been taken in attempts to discover a feasible alternative to fossil fuels. Advances have been in biofuels that serve to create a carbonneutral fuel for usage in automobiles that uses renewable biomasses (Ragauskas et al. 2006). Another field that has made numerous advancements in recent year is that of solar energy, which has increased the efficiency of solar cells to be able to convert a maximum of roughly 46% of incoming light into energy (Green et al. 2015). Research into the usage of single-walled carbon nanotubes (SWCNTs) in photovoltaic cells had essentially reached a standstill, as the efficiency of these cells were much lower than other solar cells. A photovoltaic cell is a device that takes the energy emitted by the sun and converts that into usable energy. Essentially, all solar panels are examples of photovoltaic cells. However, Gong and others (2014) were able to utilize many different types of single-walled carbon nanotubes to increase the efficiency of light to energy conversion into the range of 3%. While still lower than many other solar cells, the materials required for this solar cell are less expensive and further development can lead to increases in efficiency (Gong et al. 2014).

Carbon nanotubes are a relatively new discovery that have the potential to be used for many different applications. This is possess a result of the many different advantageous traits that the carbon nanotubes. They can be made to be stronger than steel, conduct heat extremely effectively, and are malleable enough to be formed into any shape (Gong et al. 2014). This is caused by the strong sp² bonds that link the carbon atoms together in a cylindrical structure. The chemical structure of graphite (pencil lead) is composed of numerous layers of graphene and when these individual graphene layers are separated, they can be formed into nanotubes as shown in figure 1. Depending on how the graphene is rolled, the physical properties of the nanotube can drastically change due to the configuration of the carbon atoms and their bonds.



Figure 1) The chemical structure of single-walled carbon nanotubes. The carbon atoms are arranged to form a hexagonal lattice. Modified from: http://www.tasc-nt.or.jp/en/project/characteristic.html

Due to the various traits possessed by single-walled carbon nanotubes, I hypothesize that the usage of these nanotubes in photovoltaic cells will prove to be advantageous for the production of solar energy. Their ability to absorb both infrared and visible spectrum light allows them access to a greater range of wavelengths to absorb energy. By having a large number of conformations, a wide variety of single-walled carbon nanotubes can be created. Each of these conformations have physical properties that differ between them such as tensile strength and conductivity. These different structures have the potential to lead to breakthroughs that have not been investigated or thought to be dead-ends. These factors combined with the wide range of characteristics displayed by different single-walled carbon nanotubes makes them an ideal component in photovoltaic cells.

Fabrication of Carbon Nanotubes

There are multiple ways to produce single-walled carbon nanotubes, and each produce carbon nanotubes of different diameters. Methods such as electric-arc discharges (Journet et al. 1997), laser vaporization (Lebedkin et al. 2002), and liquid plasma spray (Kim et al. 2014) are capable of producing single-walled carbon nanotubes with diameters of between 1-2 nm. It is possible to produce larger diameter variants of upwards of 6 nm (Lebedkin et al. 2006) if the need arises. Of the methods mentioned above, all of them use graphite rods and expose them to various external forces to transform them into single-walled carbon nanotubes.

For the laser vaporization method, an unfocused laser is aimed onto a carbon graphite rod composed of graphite, iron, cobalt, and nickel which is rotated in a tube heated to roughly 1200°C. The tube is filled with either pure argon gas or argon gas mixed with hydrogen. By filling the tube with the gas mixture, the formation of the single-walled carbon nanotubes takes much longer, but have a larger diameter (Lebedkin et al. 2006). The vaporized graphite arranges itself to form single-walled carbon nanotubes, which are then cooled on a collecting apparatus as shown in figure 2. These different nanotubes are of scientific interest when comparing and contrasting the differences in their properties and how they can be used. The formation of these carbon nanotubes with a larger diameter is hindered due to the decreased vaporization rate with the graphite rod in the presence of hydrogen gas. Ci and others (2001) hypothesized that this is caused by the hydrogen gas interacting with the small amount of iron particles in the original graphite sample.



Figure 2) The production of carbon nanotubes via laser vaporization. A laser is used to vaporize a graphite target. The resulting vapor is moved to the much colder collector where it is condenses and is collected. Modified from http://ipn2.epfl.ch/CHBU/NTproduction1.htm

The production of single-walled carbon nanotubes using a liquid plasma spray operates a very different way. For this method, a feedstock containing hydrocarbons and metallic catalysts is fed through an atomizer into a plasma torch containing an argon hydrogen plasma spray. The atomizer converts the feedstock into individual particles which are suspended in air as shown in figure 3a. This plasma spray is created by superheating an argon, hydrogen gas mixture until the molecules ionize, resulting in plasma. After being sprayed by the plasma that is in excess of 4000 K, the heated carbon particles are then condensed and collected via a vacuum in a filtration chamber (Figure 3b). Kim and others (2014) have reported that using a liquid feedstock instead of a solid or gaseous feedstock produces single-walled carbon nanotubes of high structural quality and purity comparable to the laser vaporization method. The production of these carbon nanotubes is continuous and 1.5-2.0 grams can be produced every hour, which has the potential for industrial-scale production (Kim et al. 2014).



Figure 3) (a) The hydrocarbon feedstock is converted into liquid droplets as they leave the atomizer. (b) The hydrocarbon feedstock is converted into droplets before being super-heated by plasma to form the carbon nanotubes. Modified from Kim et al. 2014.

Finally, the arc discharge method uses electricity instead of a laser of plasma. Instead of a single graphite rod, two graphite rods are oriented so that one acts as an anode while the other acts as a cathode and are separated by a few millimeters. Additionally, these graphite rods can be surrounded by an inert gas such as argon or helium which acts to stabilize the reaction and prevent other products from forming. When an electrical current is run between these graphite rods, a black sooty residue is produced that contains the carbon nanotubes. Journet and others (1997) used a similar process, but added a mixture of graphite powder and a metallic catalyst to a hole drilled on the anode. When an electrical current of 100 amps was run through these rods, a black soot containing bundles of single-walled carbon nanotubes was produced. Without this added mixture added to the anode, a different type of carbon nanotube would be produced that possess multiple walls instead of just a single wall.



Figure 4) The production of carbon nanotubes with the arc discharge method. When an electric current is provided, a plasma arc is created between the cathode and anode. This results in the carbon nanotubes forming and being deposited as soot in the reaction chamber. Modified from Harris PJF (2007)

Each individual method has its own advantages and drawbacks, making some methods more efficient than others. The plasma spraying method is the only one that can be continuously, which prevents unnecessary downtimes during the production of the carbon nanotubes. Table 1 highlights the advantages and disadvantages of each method discussed above and their potential yields

Method	Advantages	Disadvantages	Yield
Arc Discharge	High QualityRelatively Inexpensive	Short lengthRandom sizes produced	30-90% of starting material
Laser Vaporization	 Diameter range can be controlled Mainly SWCNT produced 	 Unwanted forms produced Equipment is expensive 	~70% of starting material
Plasma Torch	 Continuous Process Multiple SWCNTs can be produced 	 Minor defects in the SWCNTs 	1.5-2.0 g/min

Table 1) The main production methods of carbon nanotubes and the advantage and disadvantages associated with each. Since the plasma spraying method is continuous, the yield is measured as a rate, instead of a percentage of the starting materials.

Effect of Different Conformations

One of the main issues with working with carbon nanotubes and their production is that it near impossible to produce just one type of carbon nanotube. During the development process, different conformations of the single-walled carbon nanotubes are created inadvertently and the products must be sorted to isolate one particular configuration of the nanotubes. This poses an additional hurdle for the development of single-walled carbon nanotubes as additional time and resources must be put towards the separation of the various configurations that are produced in conjunction with one another.

When describing the specific configuration of a carbon nanotube, there are three different names that describe the structure: armchair, zigzag, and chiral. To determine what type a particular nanotube is, it is given a set of chiral indices (n,m) (Hároz et al. 2013). If the 'm' value is 0, and the 'n' value is anything other than 0, than it is zigzag as shown in figure 5b. When both values are the same, it is considered an armchair configuration (figure 5a). Anything else results in a chiral configuration for the nanotube (figure 5c). These values are determined by using an electron microscope.



Figure 5) The different structural conformations of single-walled carbon nanotubes walls, which are armchair (a), zigzag (b), and chiral (c). The red lines show the different orientates of the carbon bonds Modified from: http://www.intechopen.com/source/html/16801/media/image2.png

Each of these different configurations and chiral indices result in drastically different single-walled carbon nanotubes. For example, all carbon nanotubes with an armchair configuration are considered metallic and are much more conductive than other metals such as copper (Lu and Chen 2005). All other configurations result a nanotube that is essentially a semiconductor that only conducts electricity under specific conditions (Lu and Chen 2005). Therefore, it is important to consider the type of single-walled carbon nanotubes that will be used for building solar cells as some configurations are more effective than others.

Application to Solar Cells

Solar cells operate on the basis of taking incoming photons that are emitted from the sun and using it to excite electrons in the different materials used in the solar cell. Photons are packets of energy that make up all electromagnetic radiation, including visible light. When the photon enters the solar cell, it is absorbed by the electrons in the material, causing them to become excited. Once this happens, something known as an exciton is created (Liang 1970). An exciton is composed of the excited, negatively charged electron, and the now positive 'hole' that the electron once occupied (Liang 1970). Normally, the electron would orbit this positive area until the electron decays back to its initial position. When this occurs, energy is then released as another photon.

In order to harness the energy contained by these excited electrons, they must be removed from their orbit. For this to occur, the electron and the positively charged 'hole' must not fuse back together until the energy has been taken from the electron. To accomplish this, the charges are separated by using different materials, such as silicon, that will accept either the negative electron, or the positive 'hole' (Ye et al. 2014). Once the two components are effectively separated, a circuit can be set up so that they each travel to their respective electrodes. This results in a voltage that allows the electron to do a certain amount of work, which uses the energy it absorbed from the photon. With the energy effectively transferred, the electron can fuse back with the positive 'hole' and be used again.

Single-walled carbon nanotubes are an ideal candidate for solar cells as they are able to not only able to absorb the energy from incoming photons, they can also effectively transport the excited electrons (Kymakis et al. 2003). As well, the different configurations of single-walled carbon nanotubes allows each individual version to absorb energy from a different region of the electromagnetic spectrum (Rance et al. 2010). This generally ranges from infrared light, through the visible spectrum of light, and into the ultraviolet range with each separate configuration absorbing a different region. Therefore, using multiple different kinds of single-walled carbon nanotubes allows for a more effective solar cell.

Recent Applications

One of the greatest advancements in the development of successful carbon nanotube solar cells was made by Gong and others (2014). They managed to use a variety of different configurations of single-walled carbon nanotubes in conjunction with other materials to nearly double the power output of similar cells. This was accomplished through the usage of multiple carbon nanotubes that were able to absorb a wider range of incoming electromagnetic radiation. Figure 6 shows the different layers used to fabricate the solar cell.



Figure 6) The composition of the photovoltaic cell that was produced by Gong and others (2014). The multiple layers allows for a greater absorption of energy as well as effective electron transfer. Modified from Gong et al. (2014)

Another recent usage of single-walled carbon nanotubes in photovoltaic cells was by Ye and others (2014). By using a particular chiral configuration of single-walled carbon nanotubes in conjunction with poly(methyl methacrylate), they were able to produce an ultralight and porous material called aerogel. The poly(methyl methacrylate), (PMMA), was used to prevent the reflecting of light off of the carbon nanotubes, which allowed more photons to reach the single-walled carbon nanotubes. By using this aerogel as the primary component, Ye and others (2014) were able to create a solar cell that produced a voltage of 0.56 volts. The energy that was absorbed came primarily from the visible and near-infrared region of the electromagnetic spectrum and resulted in a 1.7% conversion of light to power (Ye et al. 2014).

Ending/Summary

Single-walled carbon nanotubes are an ideal candidate for usage in solar cells, although much more research must be conducted to better understand the nature of these nanotubes. Significant advancements have been made to the usage of carbon nanotubes in solar cells, with the field only beginning to be explored more in-depth after years of minimal research. Despite the many different methods for the production of the single-walled carbon nanotubes, scientists have yet to find a method of fabrication that can produce high quality nanotubes that have minimal defects, and is economically viable. Although, with relatively inexpensive and abundant amounts of material required for their production, single-walled carbon nanotubes can be made economically feasible, provided low-cost production methods emerge. As well, there are many different configurations of single-walled carbon nanotubes that can be produced in any given method. These different conformations have a wide variety of physical properties and must be separated out in order to get one particular configuration. However, the usage of multiple configurations allows for more photons to be absorbed from a wider range of the electromagnetic spectrum, resulting in greater amounts of energy. Despite the advancements made, the efficiency of solar cells utilizing single-walled carbon nanotubes has not reached the efficiency of solar cells that utilize other materials such as silicon. While this means that solar cells containing carbon nanotubes are not currently in a position to become the dominant material in all solar cells, the potential is present.

Conclusion

The discovery of carbon nanotubes opened a great many doors for their potential applications. Their wide range of properties have seen them been used in many different facets, including solar cells. While the technology is still not fully understood, scientists have been able to understand a great deal of how the carbon nanotubes are constructed and how they have their unique attributes. There are still hurdles that prevent carbon nanotubes from being used in solar cells such as economic viability and application difficulties. However, the future appears bright for their usage in photovoltaic cells and possibly becoming the fore-most material used, eclipsing all others.

Literature Cited:

- Ci L, Wei J, Wei B, Liang J, Xu C, Wu D. 2001. Carbon nanofibers and single-walled carbon nanotubes prepared by the floating catalyst method. Carbon 39(3):329-35.
- Gong M, Shastry TA, Xie Y, Bernardi M, Jasion D, Luck KA, Marks TJ, Grossman JC, Ren S, Hersam MC. 2014. Polychiral semiconducting carbon nanotube-fullerene solar cells. Nano Letters 14(9):5308-14.
- Green MA, Emery K, Hishikawa Y, Warta W, Dunlop ED. 2015. Solar cell efficiency tables (version 45). Prog Photovoltaics Res Appl 23(1):1-9.
- Harris PJF. 2007. Solid state growth mechanisms for carbon nanotubes. Carbon 45(2):229-39.
- Hároz EH, Duque JG, Tu X, Zheng M, Hight Walker AR, Hauge RH, Doorn SK, Kono J. 2013. Fundamental optical processes in armchair carbon nanotubes. Nanoscale 5(4):1411-39
- Journet C, Maser WK, Bernier P, Loiseau A, Lamy de la Chapelle M, Lefrant S, Deniard P, Lee R, Fischer JE. 1997. Large-scale production of single-walled carbon nanotubes by the electric-arc technique. Nature 388(6644):756-8.
- Kim KS, Kingston CT, Ruth D, Barnes M, Simard B. 2014. Synthesis of high quality single-walled carbon nanotubes with purity enhancement and diameter control by liquid precursor ar-H2 plasma spraying. Chem Eng J 250:331-41.
- Kymakis E, Alexandrou I, Amaratunga GAJ. 2003. High open-circuit voltage photovoltaic devices from carbon-nanotube-polymer composites. J Appl Phys 93(3):1764-8.
- Lebedkin S, Schweiss P, Renker B, Malik S, Hennrich F, Neumaier M, Stoermer C, Kappes MM. 2002. Single-wall carbon nanotubes with diameters approaching 6 nm obtained by laser vaporization. Carbon 40(3):417-23.
- Lu X and Chen Z. 2005. Curved pi-conjugation, aromaticity, and the related chemistry of small fullerenes (<C60) and single-walled carbon nanotubes. Chem Rev 105(10):3643-96.

Liang WY. 1970. Excitons. Physics Education 5(4):226-8.

- Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick Jr. WJ, Hallett JP, Leak DJ, Liotta CL, et al. 2006. The path forward for biofuels and biomaterials. Science 311(5760):484-9.
- Rance GA, Marsh DH, Nicholas RJ, Khlobystov AN. 2010. UV-vis absorption spectroscopy of carbon nanotubes: Relationship between the p-electron plasmon and nanotube diameter. Chemical Physics Letters 493(1-3):19-23.
- Ye Y, Bindl DJ, Jacobberger RM, Wu M-, Roy SS, Arnold MS. 2014. Semiconducting carbon nanotube aerogel bulk heterojunction solar cells. Small 10(16):3299-306.