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Carbon Nanotube Inkjet Printing for Flexible Electronics and Chemical Sensor Applications

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CARBON NANOTUBE INKJET PRINTING FOR FLEXIBLE ELECTRONICS AND CHEMICAL SENSOR APPLICATIONS

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ABSTRACT

Carbon nanotubes (CNTs) are becoming a promising new material for use in many fields including the field of electronics. Their mechanical and electrical properties lend themselves to be used in a new generation of electronic devices, namely flexible electronics. Although many deposition methods for carbon nanotubes exist, inkjet printing offers many advantages including superior patterning ability and low-cost fabrication. Presented in this work is the use of inkjet printing in order to deposit carbon nanotubes onto a flexible transparency film. The methods for developing and printing an aqueous single-walled carbon nanotube (SWCNT) ink and an aqueous multi-walled carbon nanotube (MWCNT) ink are discussed in detail. The carbon nanotubes are dispersed using sodium n-dodecyl sulfate (SDS), an anionic surfactant. It is discovered that the SDS:CNT ratio plays a crucial role in determining the conductivity of the printed carbon nanotube network. Thus, methods for optimizing this ratio are presented. To the author's knowledge, this is the first report of carbon nanotube ink optimization regarding the ratio of dispersant concentration to carbon nanotube concentration. Additionally, the sheet resistance and transparency of the inkjet-printed carbon nanotube films are discussed. Incredibly conductive carbon nanotube networks were printed, reaching as low as 132 Ω/☐for SWCNTs and 286 Ω/☐for MWCNTs for 35 prints. These values are among the lowest reported sheet resistance values for carbon nanotube inkjet printing. Finally, the fabrication of a fully printed electrochemical sensor using inkjet-printed carbon nanotube electrodes is presented. The sensor was characterized using cyclic voltammetry, and the results confirm that inkjet-printed carbon nanotubes are indeed a candidate for use as flexible electrodes.

1. INTRODUCTION

The purpose of this thesis is to offer insight into an emerging technology within the field of electronics. The concept of inkjet printing has been around for quite some time, but recently inkjet printing has been expanded for uses other than standard office printing. In particular, inkjet printing is being used to deposit various materials for a multitude of applications within a variety of fields. The work presented in this thesis entails the use of inkjet printing to deposit carbon nanotubes onto flexible substrates. Various applications for these carbon nanotube thin films are also discussed and demonstrated.

1.1 Overview

The work presented in this thesis merges two incredible technologies, which are truly capable of making an unbelievable impact in the field of electronics. On the one hand is a new and exciting material: carbon nanotubes. Due to their extraordinary electrical and mechanical properties, carbon nanotubes are a perfect candidate for flexible electronics. Additionally, carbon nanotubes are a cheaper alternative to other conductive metals like gold and silver. On the other hand is inkjet printing. Unlike many other forms of printing and material deposition, inkjet printing can be used to fabricate cheap and flexible devices. Using these two technologies together results in the possibility for low cost, flexible electronics and chemical sensors, both of which will be demonstrated throughout this thesis.

1.2 Research Goals

The goals of this research are:

1. To develop a conductive single-walled carbon nanotube (SWCNT) ink and multi-walled carbon nanotube (MWCNT) ink for inkjet printing;
2. To optimize the SWCNT and MWCNT inks in order to obtain the lowest possible sheet resistance;
3. To characterize the SWCNT and MWCNT inkjet-printed thin films, and
4. To fabricate and characterize a fully printed electrochemical sensor that uses inkjet-printed CNT electrodes.

The motivations behind this work are numerous. On the surface, this work was performed in order to demonstrate the fabrication of flexible electronics and sensors using inkjet printing and carbon nanotubes. However, the motivation for this work is much deeper than that. In demonstrating the development and printing of carbon nanotube ink, the door has been opened for many possibilities. The question to ask is this: “What else can be printed with an inkjet printer?” As will soon be discussed, the requirements for printing a particular material rely on a few simple ink properties, namely a good dispersion, a low surface tension, and a low viscosity. Provided the ink meets these three requirements, inkjet printing can be used for material deposition.

In terms of electronics, there are three primary materials of interest: conductors, semiconductors, and dielectrics. Using nanomaterials and polymers, it is conceivable to say that these three types of materials can be printed using inkjet printing. Thus, virtually any type of electronic device or circuit can be fabricated using inkjet printing. Although this technology would undoubtedly take time to develop, it is certainly

possible. In a sense, the information presented in this thesis lays the foundation for inkjet-printed flexible electronics and sensors.

1.3 Thesis Outline

The main body of this thesis includes a total of five chapters. This first chapter introduces the concept of carbon nanotube inkjet printing and provides an overview of the topic. Additionally, the objectives are defined and the motivation for this research is discussed.

Chapter 2 offers an extensive review of the inkjet printing technology as well as how it has been used to deposit carbon nanotubes onto various substrates. In particular, the process for developing and printing carbon nanotube ink is discussed and the characteristics of such thin films are presented. Furthermore, recent reports of carbon nanotube inkjet printing are reviewed in detail.

Chapter 3 presents the first achievements of this work including the development and printing of both SWCNT ink and MWCNT ink. Throughout the chapter, various comparisons are made between the SWCNT ink and the MWCNT ink. Additionally, two simple applications for carbon nanotube inkjet printing are demonstrated.

Chapter 4 presents an electrochemical sensor as a more complex application for this technology. In particular, inkjet-printed SWCNTs are used as electrodes for a fully printed electrochemical sensor. The process for fabricating the sensor is presented, and the experimental sensing results are shown and discussed.

Chapter 5 offers a summary of this thesis as well as necessary concluding remarks. Additionally, possible future work is discussed with the intent of proposing a

direction for continuation of the research and development of carbon nanotube ink for various applications.

2. CARBON NANOTUBE INKJET PRINTING REVIEW[1]

Carbon nanotubes (CNTs) have truly become one of the most exciting materials in recent years due to their extraordinary properties. In particular, the electrical properties of carbon nanotubes lend themselves to many applications including use in transistors [2], [3], radio-frequency identification (RFID) tags [4], sensors [5]–[9], photonics [10], [11], biological sensing labels [12], and more. One of the most interesting applications of carbon nanotubes is that of transparent electrodes. Considering indium tin oxide (ITO) is the dominant commercial material for transparent electrodes, carbon nanotubes would provide a cheaper alternative. Furthermore, not only can carbon nanotubes assist in reducing the cost of these types of electronic devices, but they can also allow these devices to become flexible.

In order to take advantage of the unique properties of carbon nanotubes, many groups have experimented with various carbon nanotube deposition methods such as dip coating [13], spray coating [3], [9], [14], [15], electrophoretic deposition [16]–[19], and others. However, one of the prominent methods of interest today is printing. There have been demonstrations of screen printing [20], aerosol printing [21]–[23], transfer printing [24], and contact printing [25] to deposit carbon nanotubes on various substrates, but the most favorable form of printing is that of inkjet printing.

Inkjet printing offers unique advantages over other methods of printing. It requires absolutely no prefabrication of templates, allowing for a rapid printing process at low cost. Additionally, due to its precise method of patterning, post-printing steps like

[1] This chapter previously appeared as R. P. Tortorich and J.-W. Choi, “Inkjet printing of carbon nanotubes,” *Nanomaterials*, vol. 3, no. 3, pp. 453-468, Jul. 2013. It is reprinted by permission of MDPI — Multidisciplinary Digital Publishing Institute [1].

photolithography are not necessary. Furthermore, multiple materials can be deposited simultaneously with the use of multiple ink cartridges, and the amount of deposited material can be controlled with great precision. Finally, due to the nature of inkjet printing technology, multiple layers can be printed on top of one another with great ease. Inkjet printing is currently being used to deposit various types of conductive nanomaterials such as gold [26], [27] and silver [28], [29]. Although these metals are excellent conductors, carbon nanotubes are cheaper and more versatile in the sense that they can behave as both a semiconductor and a conductor.

Before discussing inkjet printing as it pertains to carbon nanotube printing, it is first necessary to review the various inkjet printing technologies. In general, inkjet printing can be split into two categories, namely continuous and drop-on-demand. As suggested by its name, continuous inkjet printing supplies a continuous stream of ink droplets. These droplets are charged upon leaving the nozzle and are then deflected by voltage plates, where the applied voltage determines whether the droplet will be deposited onto the substrate or recycled through the gutter. Consequently, when the printer is not actually printing anything onto a substrate, a stream of droplets is still being ejected from the nozzle and recycled through the gutter.

While continuous inkjet printers are still used, drop-on-demand inkjet printers are more common. As opposed to a continuous inkjet printer, a drop-on-demand inkjet printer ejects a droplet of ink only when it is told to do so. Therefore, when the printer is not actually printing anything onto a substrate, there are no droplets being ejected from the nozzle. Drop-on-demand inkjet printers can be further split into two categories, namely thermal and piezoelectric. Thermal inkjet printers, sometimes referred to bubble

jet printers, contain a thin film resistor in the nozzle. In order to eject a droplet, this thin film resistor is heated by passing current through it. This causes the ink in the nozzle to vaporize, creating a bubble and a large increase in pressure, which forces ink droplets out of the nozzle. Hewlett-Packard, Canon, and Lexmark employ this type of drop-on-demand inkjet printer.

Piezoelectric inkjet printers contain a piezoelectric transducer in the nozzle. When voltage is applied to the piezoelectric transducer, it deforms and causes an increase in pressure, which forces ink droplets out of the nozzle. In terms of consumer printers, Epson employs this type of drop-on-demand inkjet printer. However, many specialized commercial inkjet printers, such as the Fujifilm Dimatix, employ the piezoelectric drop-on-demand technology as well.

Although inkjet printing has its advantages, it also has its obstacles and difficulties. The first step in inkjet printing is formulating ink. There are several issues to consider when mixing ink to be used in an inkjet printer. In general, the ink must maintain a low surface tension as well as a low viscosity. Aside from these properties, incorporating nanomaterials into an ink presents further issues, primarily due to the difficulty of dispersing the nanomaterial within the ink. More specifically, a well-dispersed nanomaterial ink should be free from flocculation of the nanomaterial within the ink. There is a great deal of current research being done on carbon nanotube dispersion, and there have been reports on dispersing carbon nanotubes in water [30]–[37] as well as organic solvents such as dimethylformamide (DMF) [30], [38], [39], N-methyl-2-pyrrolidone (NMP) [30], [39], [40], chloroform [30], [41], and others [39].

With the basics of inkjet printing covered, the specifics of carbon nanotube inkjet printing will now be discussed in the following sections. This includes carbon nanotube networks, formulation and preparation of carbon nanotube ink, and key aspects of ongoing research. Along the way, advantages and disadvantages will be discussed for varying methods.

2.1 Carbon Nanotube Network

Before reviewing both the difficulties in formulating carbon nanotube ink and the current research, it is important to first understand how inkjet printing of carbon nanotubes can be used to create conductive traces. When carbon nanotubes, or any one-dimensional nanomaterial, are printed onto a substrate, the solvent evaporates, leaving behind a random network of carbon nanotubes. This network would be analogous to dropping a handful of spaghetti onto a tabletop. Some of the spaghetti might not be in contact with any other spaghetti. In a similar way, some of the carbon nanotubes might be completely isolated without having contact with any other carbon nanotubes. In this case, electrons are confined to a single carbon nanotube. Consequently, isolated carbon nanotubes do not contribute to the conductivity of the printed film. On the other hand, some of the spaghetti may indeed be in contact with other spaghetti, just as some of the carbon nanotubes may be in contact with other carbon nanotubes. This essentially creates an electron pathway. Electrons are capable of traveling from one carbon nanotube to another, ultimately resulting in current, which is the reason for the conductivity of the printed film. Figure 2.1 demonstrates this concept.

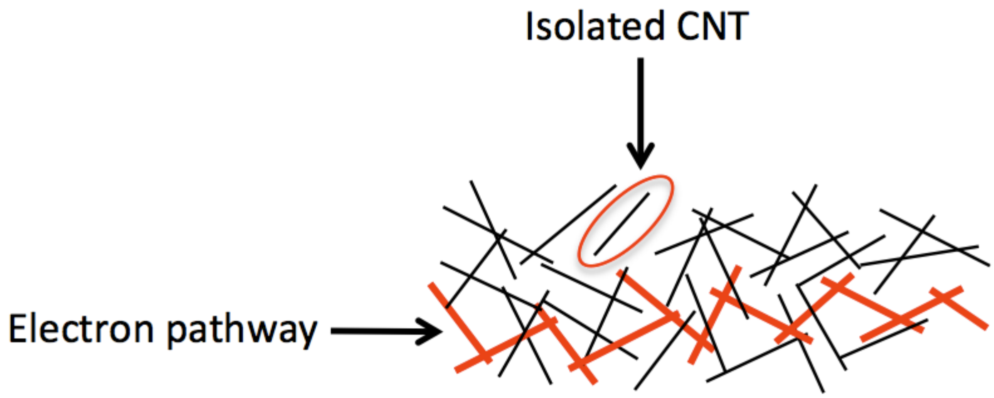


Figure 2.1 Random carbon nanotube network showing both an isolated carbon nanotube and formation of an electron pathway via overlapping carbon nanotubes.

As expected, the amount of current is directly related to the number of electron pathways. This suggests that the length of carbon nanotubes plays an important role in the conductivity of a carbon nanotube thin film. Revisiting the aforementioned pasta analogy, if the spaghetti pieces are short, the probability of them touching each other decreases. For a carbon nanotube network, this corresponds to a lower conductivity. On the contrary, if the spaghetti pieces are long, the probability of them touching increases, which corresponds to a higher conductivity in a carbon nanotube network. It will soon be shown that in order to achieve highly conductive films of carbon nanotubes by inkjet printing, it is necessary to print multiple layers of carbon nanotubes. This initially results in a substantial increase in conductivity since each additional layer of carbon nanotubes provides a denser network and produces more electron pathways. However, eventually, the conductivity of the printed film will reach the carbon nanotube bulk conductivity. Figure 2.2 shows estimated data from two recent reports on carbon nanotube inkjet printing [42], [43] as well as our own recent

test results. It should be noted that sheet resistance is plotted, which is both more common and useful than conductivity.

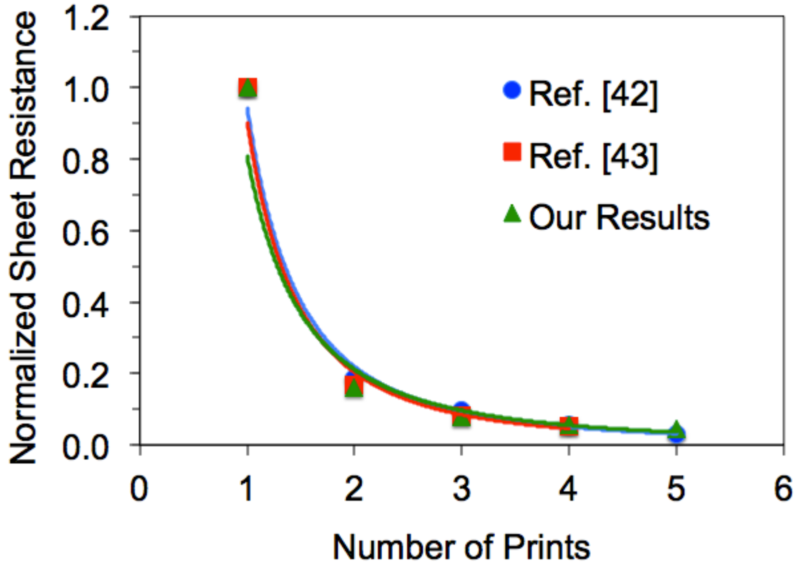


Figure 2.2 Estimated sheet resistance versus number of prints for two recent reports on carbon nanotube inkjet printing [42], [43] and our own recent test results on carbon nanotube inkjet printing. Sheet resistance values are normalized.

The bulk conductivity is determined by many factors. Here again, the length of the carbon nanotubes also plays a major role. As demonstrated by Hecht *et al*., the conductivity of a carbon nanotube network increases as the length of the carbon nanotubes increases [44]. Additionally, the type of carbon nanotubes used affects the conductivity as well, which includes single-walled or multi-walled, semiconducting or metallic, pristine or functionalized, and other variations. Furthermore, dispersants can even reduce the conductivity of carbon nanotube networks by inhibiting contact between carbon nanotubes [45]. Finally, the drying process can affect the distribution and orientation of carbon nanotubes, which will be discussed in Section 2.3.4. Nevertheless, this random network of carbon nanotubes is essential in forming a conductive thin film.

2.2 Carbon Nanotube Ink

There are many issues that need to be taken into account regarding carbon nanotube ink. First and foremost, carbon nanotube dispersion is a major obstacle. Aside from dispersion, surface tension and viscosity are important characteristics for carbon nanotube ink. Finally, preparation of carbon nanotube ink involves multiple steps to ensure well-dispersed carbon nanotubes and removal of any carbon nanotube bundles.

2.2.1 Carbon Nanotube Dispersion

Due to the nature of the material, carbon nanotubes are quite difficult to disperse in a liquid. The van der Waals forces between carbon nanotubes can easily cause agglomeration and sedimentation, which is highly undesirable due to the possibility of clogging the inkjet nozzle. As a result, many groups have experimented with various methods of carbon nanotube dispersion through the use of sidewall functionalization, organic solvents, and dispersants in the case of water-based ink.

2.2.1.1 Functionalized Carbon Nanotube Dispersion

The first method for carbon nanotube dispersion is that of sidewall functionalization. This entails a chemical process whereby molecules are bound to the carbon nanotube sidewalls. One of the most common methods of carbon nanotube functionalization used to enhance dispersion is called carboxylation. In carboxylation, carboxyl groups (–COOH) are attached to the sidewalls of carbon nanotubes through a series of chemical steps. Unlike the hydrophobic carbon nanotube sidewalls, these

carboxyl groups are hydrophilic, reducing the possibility for carbon nanotube bundling. On the downside, the chemical steps necessary for functionalization tend to introduce defects into the carbon nanotube sidewalls. This effectively decreases the conductivity of the carbon nanotubes. Nevertheless, a few groups have successfully formulated and printed carbon nanotube ink using functionalized carbon nanotubes [45]–[47].

2.2.1.2 Organic Solvent-Based Carbon Nanotube Dispersion

In order to avoid hindering the conductive nature of carbon nanotubes, other means of dispersion can be used. For example, organic solvents are superb in their ability to disperse carbon nanotubes. There is no need for functionalization of the carbon nanotube sidewalls or addition of other materials to enhance dispersion. Rather, the solvent itself works as a dispersant. The organic solvent molecules adsorb onto the carbon nanotube surface due to a hydrophobic interaction, countering the strong van der Waals forces between the nanotubes [38]. Additionally, due to their inherent low surface tension, there is no need to add a wetting agent to organic solvent-based inks. On the contrary, many organic solvents present some issues for practical use. First, it has been reported that organic solvents have a carbon nanotube concentration limit of approximately 0.1 mg/ml [48]. Organic solvents also tend to be quite volatile, which can cause problems both when the ink is being prepared and when the ink is being used in a cartridge. Unless the cartridge is sealed properly, the solvent will evaporate, leaving behind nothing but the carbon nanotubes and ultimately clogging the nozzle. Another problem encountered when dealing with organic solvents is that of health and environmental effects. If the proper precautions are not taken, there may be some

serious consequences. Lastly, organic solvents can be very corrosive to certain polymer materials. As a result, cartridges used for organic solvent-based carbon nanotube ink must be made of materials that resist their corrosive property. This corrosive characteristic also limits the substrate selection for organic solvent-based carbon nanotube inks. Despite the difficulties, many groups have successfully developed and printed carbon nanotube inks using organic solvents such as DMF [4], [42], [49]–[52] and NMP [53].

2.2.1.3 Water-Based Carbon Nanotube Dispersion

In addition to organic solvent-based carbon nanotube inks, some groups have developed and printed water-based carbon nanotube inks with the use of dispersants rather than functionalization of the carbon nanotubes [43], [54]–[58]. These water-based inks are environmentally friendly, easy to store, and safer to handle. However, water-based inks are much more difficult to develop since carbon nanotubes do not readily disperse in water without the aid of additional dispersants. As the surface of carbon nanotubes is hydrophobic, the nanotubes do not want to be in contact with water. Rather, they bundle together due to the attractive van der Waals forces.

There are a few ways to overcome these strong van der Waals forces. Aside from sidewall functionalization, surfactants and polymers can be used to cover the surface of each carbon nanotube in order to negate the strong van der Waals forces. This is achieved through both physical and chemical means. Surfactants are amphiphilic molecules having a hydrophilic head and a hydrophobic tail. Thus, when a surfactant is introduced into a water-based carbon nanotube ink, the surfactant

molecules adsorb onto the surface of each carbon nanotube due to the hydrophobic tail. This essentially forms a barrier around the perimeter of the carbon nanotube, which acts as the physical means to negate the van der Waals forces when carbon nanotubes are in close proximity to each other. Additionally, because the outer layer of the surfactant-covered carbon nanotube consists of the hydrophilic heads, there is a repulsive chemical force between each carbon nanotube. Polymers, on the other hand, are long chains of monomers that wrap around the carbon nanotubes forming a helix. In a similar fashion to surfactants, polymers provide both a physical and a chemical means for overcoming the van der Waals forces. Figure 2.3 briefly illustrates how surfactants adsorb onto the carbon nanotube surface.

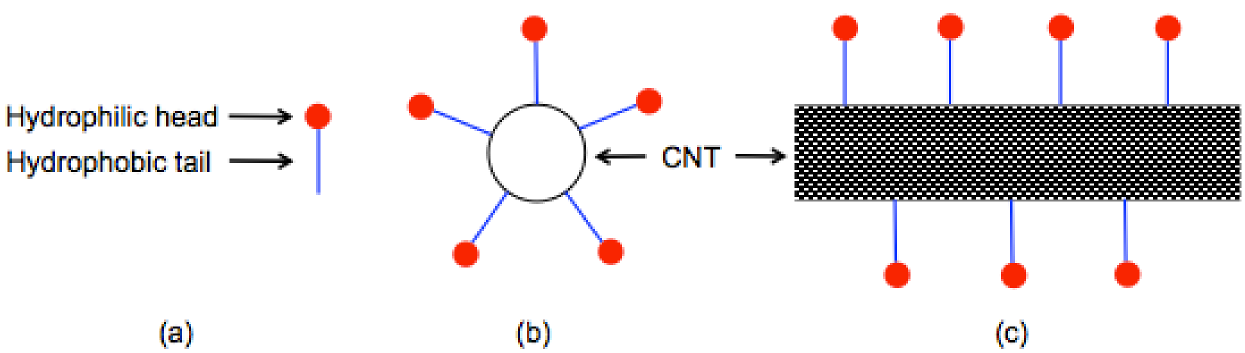


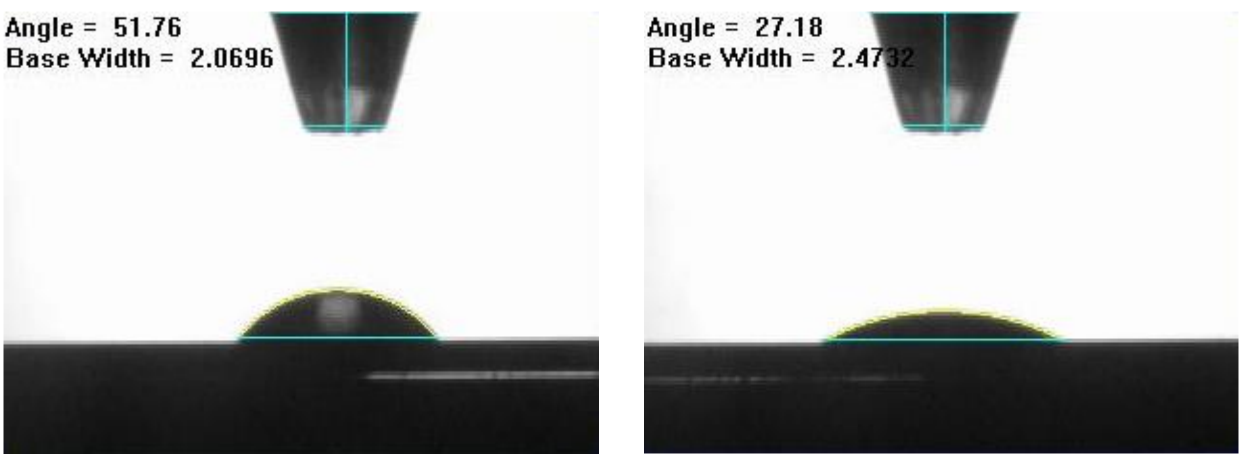
Figure 2.3 Surfactant-assisted dispersion of carbon nanotubes: (a) amphiphilic surfactant molecule; (b) cross-section of carbon nanotube covered with surfactant molecules, and (c) side view of carbon nanotube covered with surfactant molecules.

2.2.2 Carbon Nanotube Ink Surface Tension

In order for an ink droplet to be ejected from the nozzle, the ink must maintain a low surface tension. Due to the extremely small volume of ink being ejected from the nozzle (in the pl range), a low surface tension is absolutely necessary. If the surface

tension is too high, the ink droplets may remain in the nozzle of the cartridge, which is highly undesirable.

As mentioned in Section 2.2.1.2, organic solvents already have a low surface tension, so they do not require the addition of wetting agents. However, unlike organic solvents, water has a very high surface tension, resulting from the strong cohesive interaction between water molecules. In order to combat this high surface tension, wetting agents are used to lower the surface tension. Typically, surfactants are used as the wetting agent in carbon nanotube inks. In a liquid like water, the surfactant molecules accumulate on the water-air interface due to their amphiphilic structure. This ultimately reduces the cohesive forces between water molecules at the surface, which results in lower surface tension, allowing the water to spread out more on a given surface as shown in Figure 2.4.



(a) (b)

Figure 2.4 Effect of surfactant on surface tension: (a) 3 µl droplet of water without surfactant and (b) 3 µl droplet of water with surfactant. Surfactant clearly decreases the surface tension of the droplet.

2.2.3 Carbon Nanotube Ink Preparation

After determining the ingredients and relative concentrations for the carbon nanotube ink, a series of steps are performed in order to obtain useable ink. First, the ink needs to be mixed in order to disperse the carbon nanotubes within the liquid. This can be done in multiple ways, but the most common approach for dispersing carbon nanotubes is sonication, which uses high frequency vibrations to separate carbon nanotubes within a liquid. Although it works very well, this method also has its drawbacks. In particular, sonication can both shorten carbon nanotubes and cause defects. In the former case, shorter carbon nanotubes reduce the probability of forming an electron pathway in a carbon nanotube network, which can decrease the conductivity of the printed film. In the latter case, defects can negatively affect the inherent conductivity of the carbon nanotubes. Finally, sonication can both physically and chemically affect the solvent and dispersants used in a carbon nanotube ink [48]. Nevertheless, sonication seems to be the primary method of choice for carbon nanotube dispersion.

After dispersing the carbon nanotubes, the ink is centrifuged in order to separate the well-dispersed carbon nanotubes from the bundles or agglomerations, which could clog the printer nozzle. The supernatant solution is then collected and may be centrifuged again. Sometimes, the carbon nanotube ink is also filtered in order to further remove any bundles of carbon nanotubes that could clog the printer nozzle. The filtering step may be performed multiple times to ensure a uniform and well-dispersed carbon nanotube ink. Once the ink is formulated, it is loaded into an inkjet cartridge and ready to be printed.

2.3 Carbon Nanotube Inkjet Printing

One of the earlier demonstrations of carbon nanotube inkjet printing was reported by Fan *et al*. in 2005 [43], but one of the more recognized works was reported by Kordás *et al*. in 2006 [47]. Since then, there have been numerous displays of carbon nanotube inkjet printing, all of which have been successful in producing conductive carbon nanotube films. Rather than providing an exhausting review of each and every demonstration, a few key aspects of current research are discussed in this section.

2.3.1 Inkjet Printers

As stated previously, there are multiple types of inkjet printers, and all of them have been used for carbon nanotube printing. Consumer inkjet printers are quite cheap and offer familiarity, so there is no need to learn new software or hardware. Nevertheless, these printers are made to print a specific type of ink, so developing useable ink can be a bit more difficult. The new ink must match the original ink in all aspects. Furthermore, in the instance where a new ink clogs the nozzle, some consumer inkjet printers are easier to clean than others. In general, each Hewlett-Packard printer cartridge has its own nozzle, allowing the user to easily remove the cartridge and clean it. On the other hand, the nozzle for Epson printer cartridges is built into the printer itself and cannot be easily removed for cleaning. The most prominent disadvantage for consumer inkjet printers is their overall lack of control. In particular, the drop volume and spacing cannot be adjusted, and the resolution is relatively low. Regardless of these issues, there have been successful demonstrations of printing carbon nanotubes with consumer inkjet printers.

Commercial inkjet printers like the popular Fujifilm Dimatix are specifically made for printing various types of materials. As a result, they have a great deal of control over drop volume and spacing, and they provide better resolution. Although these specialized inkjet printers can be expensive, they seem to be a good choice for carbon nanotube printing due to their superior functionality.

2.3.2 Carbon Nanotube Sheet Resistance

In order for carbon nanotube films to replace other metallic conductors, they must maintain a comparable sheet resistance. Some groups were able to achieve a sheet resistance below 1 kΩ/□ using multiple layers of carbon nanotubes, the lowest being 78 Ω/□ with a total of 200 prints demonstrated by Chen *et al* [57]. Although this is a very low sheet resistance, performing 200 prints is not ideal. Taking the print number into account, the lowest recorded sheet resistance is 760 Ω/□ with a total of 12 prints [54].

One key factor that can play a major role in sheet resistance is that of dispersants. As mentioned in Section 2.1, dispersants can reduce the conductivity of carbon nanotube thin films. When dispersants are used in carbon nanotube ink, they form a physical barrier around the carbon nanotubes. Thus, in a carbon nanotube network, these dispersants can inhibit the contact between carbon nanotubes, possibly resulting in a very large decrease in conductivity. In order to diminish this effect, the dispersant concentration can be decreased. Consequently, there may be a reduction in the amount of dispersant that covers each nanotube, allowing for better contact between carbon nanotubes. On the contrary, decreasing the dispersant concentration can also result in a lower concentration of carbon nanotubes, which subsequently

decreases the conductivity. As a result, for a given type and concentration of carbon nanotubes, there seems to exist an optimum dispersant concentration that will yield the lowest possible sheet resistance.

Another possible way to prevent dispersants from reducing the conductivity is by simply removing them. Many dispersants are soluble in water and other liquids. By placing the substrate into one of these solvents, the dispersants may detach from the carbon nanotubes and dissolve into the liquid. It should be noted that during this process, some carbon nanotubes might detach from the substrate as well and disperse in the solvent, which can significantly reduce the conductivity.

2.3.3 Carbon Nanotube Transparency

Aside from sheet resistance, in order for carbon nanotube films to replace transparent electrodes like indium tin oxide (ITO), they must maintain a comparable transparency. This involves a delicate balance because increasing the conductivity through multiple prints directly affects the transparency. As more and more carbon nanotubes are deposited onto a given substrate, the film becomes less and less transparent. Although Chen *et al*. were able to achieve a very low sheet resistance, the transmittance was only 10% [57]. To the author's knowledge, there has not been a report of carbon nanotube inkjet printing that demonstrates both good sheet resistance and good transparency. However, Mustonen *et al*. did accomplish this task using a composite ink made of carboxyl functionalized single-walled carbon nanotubes (SWCNT-COOHs) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

(PEDOT-PSS) [59]. With 25 prints, the conductive film reached a sheet resistance of 1 kΩ/□ and a transmittance of 70%.

2.3.4 Carbon Nanotube Coffee Stain Effect

The well-known phenomenon denoted as the coffee stain effect occurs as a droplet of ink dries on the substrate. During drying, carbon nanotubes are pushed to the perimeter of the droplet due to an internal flux [60]. Denneulin *et al*. even demonstrated that carbon nanotubes orient themselves in specific directions at the perimeter of a drying ink droplet [61]. In order to overcome this, Denneulin *et al*. used a SWCNT-COOH/PEDOT-PSS composite ink. Other methods for limiting the coffee stain effect include heating the substrate and treating the substrate surface, which can both accelerate the drying process [42]. This helps to prevent flocculation of carbon nanotubes, allowing for a more uniform distribution and ultimately a more conductive film.

Seeing that carbon nanotube inkjet printing is quite involved, Table 2.1 on the following two pages provides a side-by-side comparison of recent reports on carbon nanotube inkjet printing. Table 2.1 includes information such as the printer used, the ink ingredients and preparation, and the sheet resistance if reported. For consistency, concentrations that were reported as a weight percent were converted to a mass per volume value (*i.e.*, μg/ml or mg/ml). Also, the table has been organized into three sections based on how the carbon nanotubes were dispersed, namely functionalization, organic solvent, or water with a dispersant.

Table 2.1 Comprehensive comparison of recently reported carbon nanotube printing.

Reference Number	Cited Papers	Printer	Solvent	Dispersant and Concentration	CNT Type and Concentration	Preparation	Best Sheet Resistance	Notable Feature
[47]	[43]	Canon	Water	Functionalized	MWCNT-COOH 0.26 mg/ml	Sonication Stirring Centrifuge	40 kΩ/□ 90 prints	One of the first reported
[46]	[47], [59]	Dimatix	Water	Functionalized	SWCNT-COOH 0.1 mg/ml	Sonication Centrifuge	Not reported	FET-like behavior
[45]	[46], [47], [53]	Dimatix	Water	Functionalized	SWCNT-COOH (carboxylic acid) SWCNT-$CONH_2$ (amide) SWCNT-PEG (polyethylene glycol) SWCNT-PABS (polyaminobenzene sulfonic acid) 0.13 mg/ml	Sonication Centrifuge	Estimated 2 kΩ/□ (for COOH and PABS) 14 prints (Assumed)	Fully inkjet printed FET
[50]	-	MicroJet	DMF	n/a	SWCNT 20 µg/ml	Centrifuge	Not reported	Gas sensing
[51]	-	MicroJet	DMF	n/a	SWCNT 0.01 mg/ml	Sonication	Not reported	Field emission display
[4]	[42], [50]	Dimatix	DMF	n/a	SWCNT 0.4 mg/ml	Sonication	Estimated 150 Ω/□ 25 prints	RFID and gas detection
[42]	[47]	MicroJet	DMF	n/a	SWCNT 0.02 mg/ml	Centrifuge	Estimated 333 Ω/□ 8 prints	Uniform CNT network
[49]	[52], [62]	MicroJet	DMF	n/a	SWCNT 0.001 µg/ml or 0.04 µg/ml (Assumed)	Sonication Filtering	Not reported	Doping of CNT Films

Table 2.1 (Cont.)

Reference Number	Cited Papers	Printer	Solvent	Dispersant and Concentration	CNT Type and Concentration	Preparation	Best Sheet Resistance	Notable Feature
[52]	[46], [47], [53]	MicroJet	DMF	n/a	SWCNT 0.001 µg/ml or 0.04 µg/ml	Sonication Centrifuge Filtering	Not reported	Fully inkjet printed FET
[53]	[47]	Microdrop Autodrop	NMP	n/a	SWCNT 0.003 mg/ml	Sonication Centrifuge Filtering	Not reported	Use of CNT as active layer in TFT
[43]	-	Not reported	Water	Special dispersant S27000	MWCNT 3 mg/ml	Centrifuge Sonication	11.6 kΩ/□ 4 prints	One of the first reported
[56]	-	HP	Water	Gellan gum or xanthan gum <1 mg/ml	SWCNT or MWCNT Concentration not reported	Sonication	Not reported	Water vapor detection
[57]	[42], [47], [63]	Epson	Water	SDS 10 mg/ml	SWCNT 0.2 mg/ml	Sonication Centrifuge	78 Ω/□ 200 prints	Supercapacitors
[54]	[43], [45], [47], [55], [61], [64]	Epson	Water	Combination of 3 different dispersants 150 mg/ml	MWCNT 0.15 mg/ml	Mixing Ball-milling Centrifuge	760 Ω/□ 12 prints	Low sheet resistance
[55]	[42], [43], [47], [51], [53], [56], [63]	Microfab	Water	Solsperce® 46000 5 mg/ml Byk 348 1 mg/ml	MWCNT 10 mg/ml	Sonication	Not reported	Electroluminescent device

2.4 Conclusion

Although carbon nanotube inkjet printing is relatively new, it seems to be a very promising method for deposition. Of course, there are a few obstacles to overcome before inkjet printing will become a commercial method for depositing carbon nanotubes, but it will not take long. With ongoing research in the area of carbon nanotube dispersion, stable carbon nanotube inks will soon be available. Furthermore, commercial inkjet printers like the Fujifilm Dimatix offer better control and resolution than general office inkjet printers. Takagi *et al.* have even demonstrated a method for further enhancing inkjet printing resolution by substrate surface modification [65]. In terms of applications, carbon nanotube inkjet printing can be used to fabricate transistors [45], [52], [53], sensors [4], [50], electroluminescent devices [55], and more. Also, given the current progress, carbon nanotubes seem to be a potential candidate for next generation printable, flexible, and transparent electrodes.

3. CARBON NANOTUBE INK PREPARATION AND PRINTING

After performing an extensive literature review, it was then time to develop and print a carbon nanotube ink. This process was quite time consuming due to many factors. As discussed in Chapter 2, the properties of the ink had to meet certain criteria in order to print correctly. After successfully developing and printing a carbon nanotube ink, it was necessary to optimize the ink concentrations in order to obtain the most conductive carbon nanotube thin films. This chapter discusses the process for developing, printing, and optimizing both single-walled carbon nanotube (SWCNT) ink and multi-walled carbon nanotube (MWCNT) ink.

3.1 Introduction

As discussed in Section 2.2, there are three properties that a carbon nanotube ink must possess in order to be used for inkjet printing. These properties include a good dispersion, a low surface tension, and a low viscosity. Due to their volatile and sometimes corrosive nature, organic solvents were not used. Instead, a water-based carbon nanotube ink was developed. Additionally, rather than using chemical functionalization as a means for carbon nanotube dispersion, a separate dispersant was used in order to obtain a highly concentrated carbon nanotube dispersion while also maintaining the structural integrity of the nanotubes, allowing for the highest possible conductivity. Please note that carboxylated multi-walled carbon nanotubes (MWCNT-COOH) were used rather than pristine MWCNTs due to availability. Although this type of functionalization does assist in carbon nanotube dispersion, the addition of a

separate dispersant provides a much better carbon nanotube dispersion and allows for the production of highly concentrated carbon nanotube ink.

3.2 Carbon Nanotube Ink

Throughout the chapter, various comparisons between SWCNT ink and MWCNT ink will be made. This comparison, of course, is not ideal, and further investigation is necessary. An ideal comparison would require the exact same number and length of carbon nanotubes, which would be very difficult to obtain for multiple reasons. Controlling the specific length during carbon nanotube growth is no easy task. On the other hand, the nanotubes can be sorted by length after growth, but this of course increases cost. Additionally, considering SWCNTs and MWCNTs of the same length have different weights, it would be necessary to determine the number of carbon nanotubes per unit mass, which would be quite difficult as well. Aside from number and length, an ideal comparison would also require the same processing steps and chirality, both of which can affect the intrinsic carbon nanotube conductivity. In any case, the comparisons offered in this chapter do indeed offer significant insight into the differences between SWCNT ink and MWCNT ink for the purpose of inkjet printing.

3.2.1 Ink Preparation and Printing

All of the carbon nanotubes were purchased from Cheap Tubes, Inc. (Brattleboro, Vermont). In particular, pristine SWCNTs with 90% purity were used, and carboxylated MWCNTs with 95% purity were used. As a dispersant, sodium n-dodecyl sulfate (SDS), an anionic surfactant, was used. The SDS was purchased from Alfa

Aesar (Ward Hill, Massachusetts). Now, before discussing the ink preparation process, it is important to truly understand the necessity for a dispersant. Although the hydrophobic nature of carbon nanotubes was discussed in Section 2.2, a visual display is helpful. As a supplement to the previous discussion, Figure 3.1 demonstrates a bad dispersion of carbon nanotubes due to the absence of a dispersant. As a result, the carbon nanotubes flocculate together and settle to the bottom of the solution.

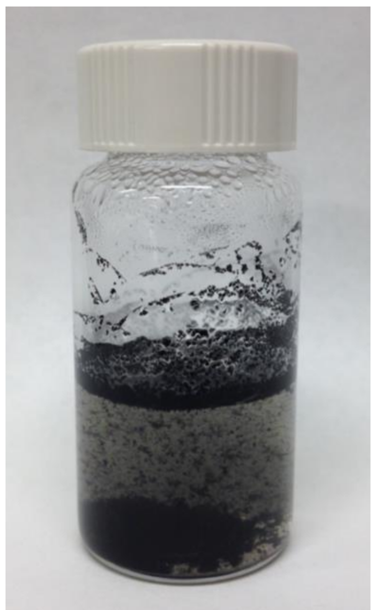
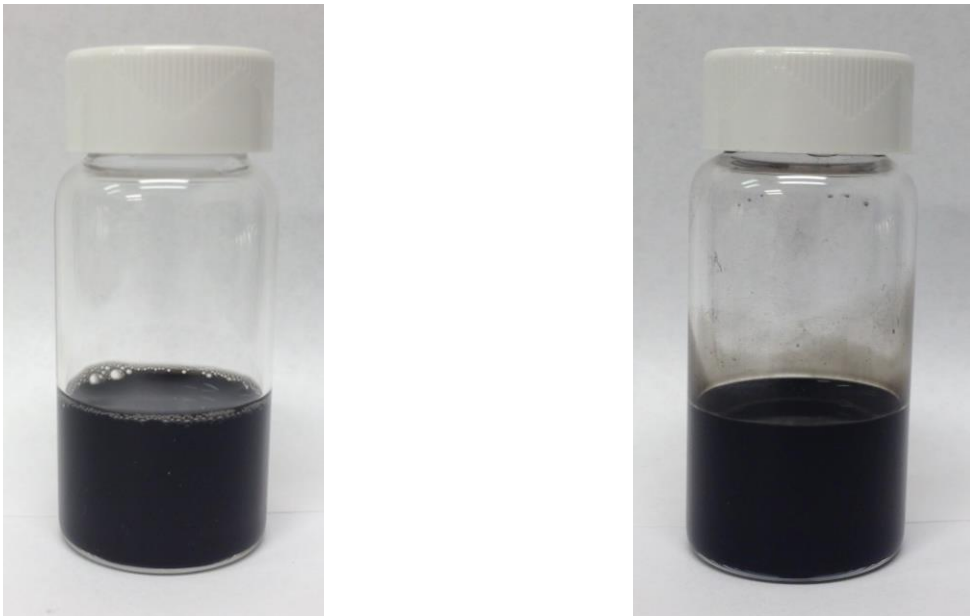


Figure 3.1 An optical image of a bottle of SWCNT ink without a dispersant (SWCNT: 0.2 mg/ml). This picture was taken immediately following a 30 minutes sonication period.

As demonstrated by the figure, the addition of a dispersant is necessary in order obtain a stable carbon nanotube ink. The process for preparing carbon nanotube ink was quite simple and did not vary between different types of carbon nanotubes. First, the desired amount of carbon nanotubes was measured using an analytical balance (HR-60, A&D) and placed into a 20 ml glass bottle. Additionally, the desired amount of

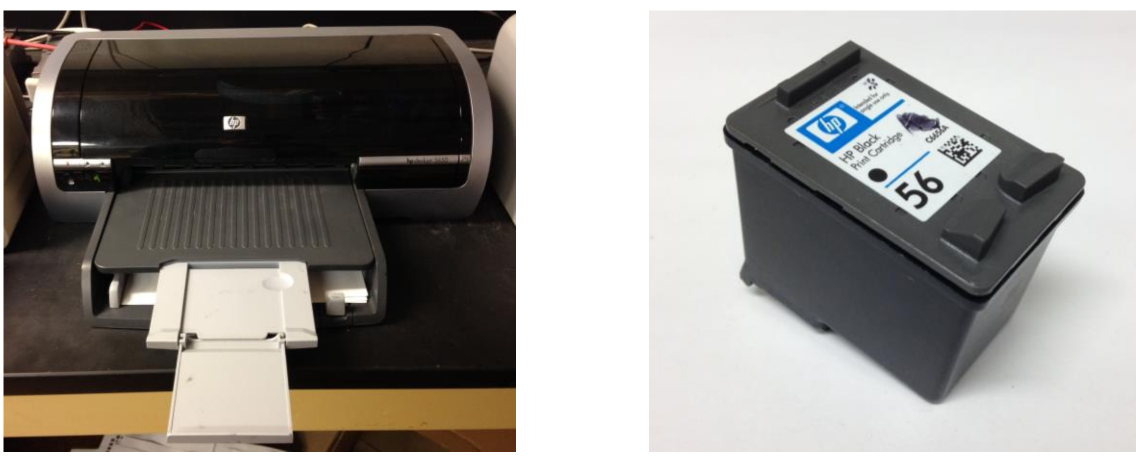
SDS was measured and placed into the same bottle. Following this measurement, the appropriate amount of deionized water (DI) was placed in the bottle as well. Next, the bottle was sonicated using a bath sonicator (FS20D, Fisher Scientific) for 30 minutes. After sonication, the carbon nanotube ink was centrifuged (MiniSpin, Eppendorf) for 5 minutes at 12,000 rpm. The supernatant was then collected. At this point, the ink preparation was complete. However, in order to verify that the ink would print properly, the contact angle was measured (FTA125, First Ten Angstroms). This measurement ensured that the ink had a low surface tension, allowing for consistent printing. To measure the contact angle, a 2 μl droplet of ink was placed on an untreated bare silicon substrate using a micropipette. Typically, a contact angle below 15° allowed for uniform and consistent printing. After confirming the surface tension was low enough, the carbon nanotube ink was injected into a clean ink cartridge and loaded into the printer. The carbon nanotube inks were printed on transparency films purchased from Inkpress. Figure 3.2 shows images of the bottled SWCNT ink and MWCNT ink.

The printer choice for this work was crucial. Commercial inkjet printers like the Fujifilm Dimatix are very expensive, and current consumer inkjet printers use very complicated multi-compartment ink cartridges and monitor them very closely. This, of course, makes it very difficult to modify a current consumer inkjet printer for printing anything other than the standard black and colored inks. Thus, for low cost fabrication and ease of use, an old consumer inkjet printer was acquired, namely the Hewlett-Packard (HP) Deskjet 5650 inkjet printer. This printer uses very simple cartridges (HP 56) that contain a single compartment, allowing for easy cleaning and ink injection. Figure 3.3 shows images of both the printer and the cartridge.



(a) (b)

Figure 3.2 Carbon nanotube ink: (a) Optical image of bottled SWCNT ink (SWCNT: 0.8 mg/ml, SDS: 3 mg/ml) and (b) Optical image of bottled MWCNT ink (MWCNT: 10 mg/ml, SDS: 7 mg/ml).



(a) (b)

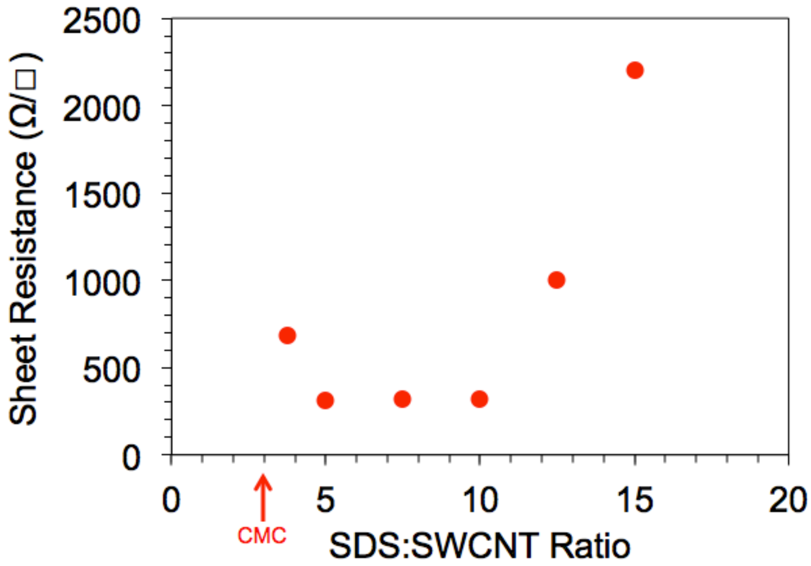
Figure 3.3 Inkjet printer and cartridge: (a) optical image of the HP Deskjet 5650 inkjet printer and (b) optical image of the HP 56 ink cartridge.

3.2.2 Optimization

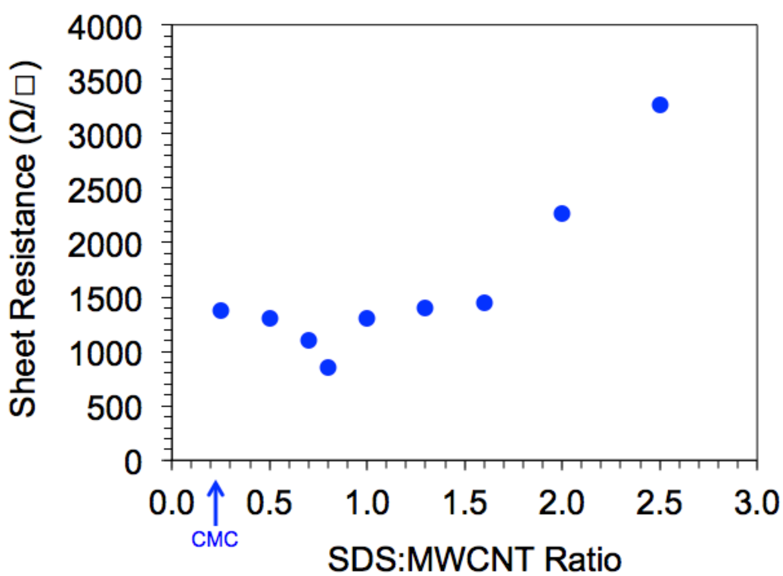
As mentioned in Section 2.3.2, there seems to exist an optimum ratio between the SDS concentration and the carbon nanotube concentration. Thus, after successfully developing and printing carbon nanotube ink, the next task was optimization. This optimization process was actually quite simple. Multiple inks were prepared, which contained the same carbon nanotube concentration but varying SDS concentrations. Each ink was printed five times on a transparency film, and the sheet resistance was measured. The same steps were followed for both the SWCNT ink and the MWCNT ink. However, as expected, the carbon nanotube concentrations differed between the two different inks. Figure 3.4 shows the optimization data for both inks.

In order to fully understand these curves, a bit of information regarding surfactants is necessary. Every surfactant has what is called a critical micelle concentration (CMC). For concentration equal to or greater than the CMC, surfactant molecules begin forming spherical micelles, where the hydrophobic tails point towards the center of the sphere while the hydrophilic heads make up the surface of the sphere. For SDS in water, this concentration is 8.2 mM, or approximately 2.37 mg/ml, as indicated in the graphs in Figure 3.4. When preparing ink near or below this concentration of SDS, both a higher surface tension and a visibly inferior dispersion were observed after centrifuging, preventing the possibility for printing.

For SDS concentrations greater than the CMC, printing was successful. As illustrated in the graphs in Figure 3.4, there seems to be a range of suitable SDS:CNT ratios for which the sheet resistance is lowest and nearly unchanged. Although further investigation is necessary, there is a likely explanation for the nearly constant sheet



(a)



(b)

Figure 3.4 Carbon nanotube ink optimization data: (a) SWCNT ink (SWCNT: 0.8 mg/ml) and (b) MWCNT ink (MWCNT: 10 mg/ml). SDS critical micelle concentration (CMC) is designated with an arrow (2.37 mg/ml).

resistance over a given range, and it is linked to the CMC. The low sheet resistance variation suggests that for a particular range, the total number of dispersed carbon nanotubes is approximately constant. The excess SDS molecules (i.e. those exceeding the CMC), however, do not contribute to further carbon nanotube dispersion. Rather, they form micelles within the solution. Thus, after centrifuging the ink, the number of dispersed carbon nanotubes per unit volume remains approximately unchanged.

For SDS concentrations much greater than the CMC, printing is successful, but there is a strange occurrence. Rather than maintaining a nearly constant sheet resistance, the sheet resistance value actually increases. This was originally attributed to increased contact resistance between the nanotubes due to large amounts of SDS inhibiting nanotube-to-nanotube contact. Although increased contact resistance is still a factor, there seems to be another explanation. It was observed that, for SDS concentrations much greater than the CMC, the printed carbon nanotube films were actually more visibly transparent than the printed carbon nanotube films with a lower SDS concentration. This suggests that the number of dispersed carbon nanotubes per unit volume effectively decreased with higher SDS concentrations. Here again, further investigation is necessary, but it is likely that, due to an excessive amount of SDS, the surfactant molecules are forming even more micelles rather than contributing to further carbon nanotube dispersion. In Chapter 5, future work regarding this occurrence will be discussed.

It should be noted that both sets of optimization data should resemble the same shape for any given carbon nanotube concentration of the same type, provided the SDS:CNT ratios are maintained. However, higher carbon nanotube concentrations will

shift the curve down (i.e. lower sheet resistance), and lower carbon nanotube concentrations will shift the curve up (i.e. higher sheet resistance).

As a visual comparison between the SWCNT prints and the MWCNT prints, Figure 3.5 shows an image of each ink printed 1-5 times on a transparency film.

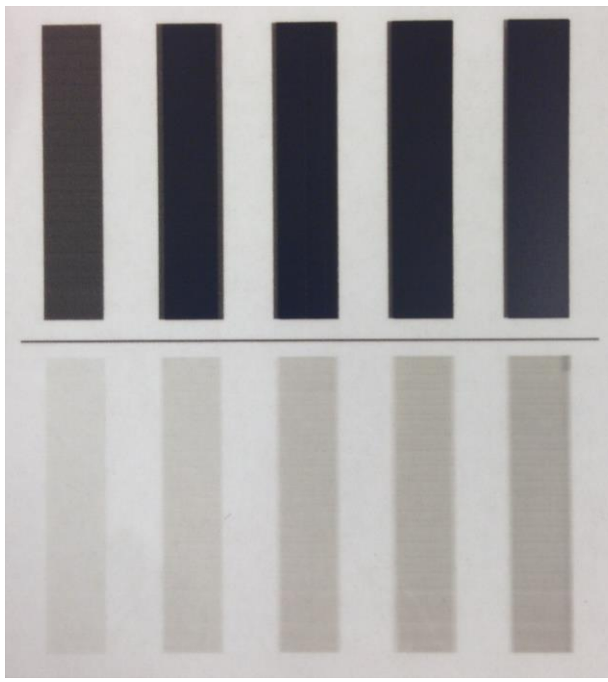


Figure 3.5 Optimized carbon nanotube inks: (top) 1-5 prints of MWCNT ink (MWCNT: 10 mg/ml, SDS: 7 mg/ml) and (bottom) 1-5 prints of SWCNT ink (SWCNT: 0.8 mg/ml, SDS: 3 mg/ml). The width and spacing of the patterns are 5 mm.

As shown in Figure 3.5, the SWCNT traces are much more transparent than the MWCNT traces. This is likely due to difference in diameter between the two types of carbon nanotubes. As designated by the manufacturer, the SWCNTs have a diameter of 1-4 nm, while the MWCNTs have a diameter of 20-30 nm. This is an incredibly significant size difference. Due to the small diameter of the SWCNTs, the network

allows a large amount of light to pass through the film. In contrast, due to the large diameter of the MWCNTs, the network blocks most of the light from passing through.

3.2.3 Sheet Resistance

After determining the optimum ratios, both inks were printed many times on a transparency film in order to determine the lowest possible sheet resistance. Initially, there is a substantial decay in sheet resistance as discussed in Section 2.1. However, after multiple prints over the same area, the sheet resistance begins to approach the bulk resistance value. Figure 3.6 shows sheet resistance curves for both SWCNT ink and MWCNT ink on transparency films.

As demonstrated by the curves in Figure 3.6, the SWCNT ink is more conductive than the MWCNT ink. The lowest sheet resistance obtained for the SWCNTs is 132 Ω/□, and the lowest sheet resistance obtained for the MWCNTs is 286 Ω/□, both of which are very conductive and among the lowest reported sheet resistance values for carbon nanotube inkjet printing (see Table 2.1 for reported sheet resistance values). Please note that this data does not show that SWCNTs are more conductive than MWCNTs. The sheet resistance value is determined by many factors, one of which being the total number of printed nanotubes. Taking into account weight per nanotube, it is likely that a concentration of 0.8 mg/ml of SWCNTs contains more carbon nanotubes than a concentration of 10 mg/ml of MWCNTs. Furthermore, the MWCNTs are functionalized unlike the pristine SWCNT, which can affect the intrinsic nanotube conductivity. In any case, both printed films show superb conductivity, confirming the possibility for using inkjet-printed carbon nanotubes as conductive electrodes.

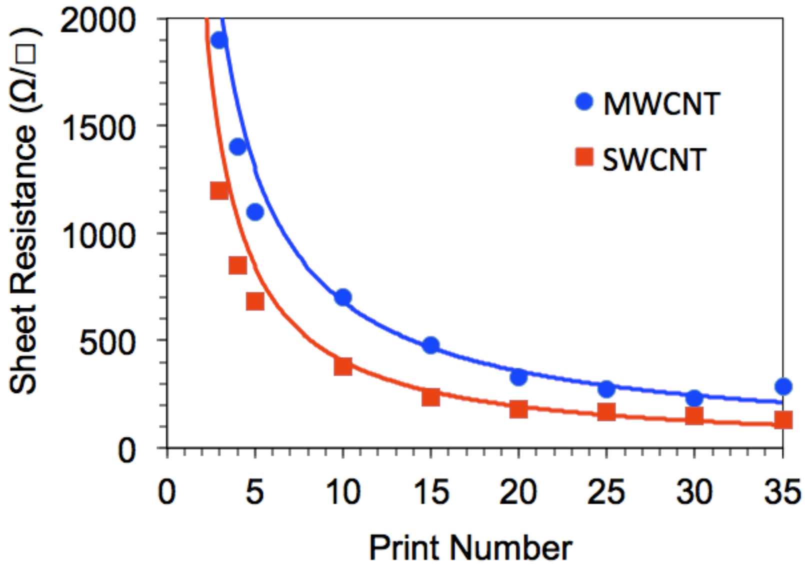


Figure 3.6: SWCNT ink (SWCNT: 0.8 mg/ml, SDS: 3 mg/ml) and MWCNT ink (MWCNT: 10 mg/ml, SDS: 7 mg/ml) sheet resistance values on transparency film for 1-35 prints.

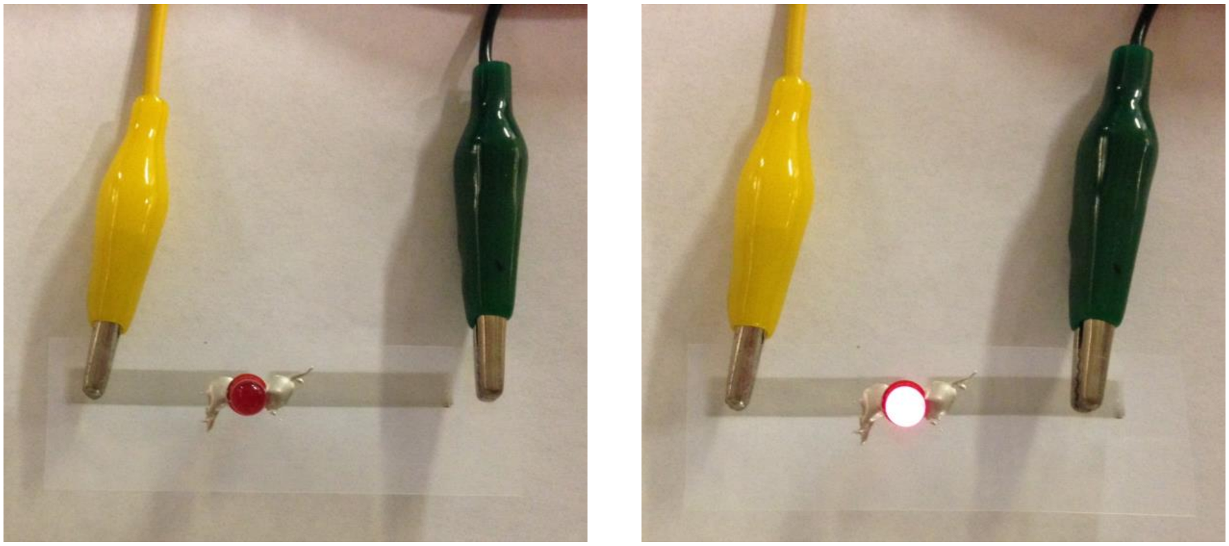
3.3 Potential Applications

Due to the nature of the material, carbon nanotubes allow for high flexibility when used with the proper substrate such as the transparencies discussed in this chapter. Thus, inkjet-printed carbon nanotubes are a potential candidate for use in flexible electronics. Although the concept of flexible electronics has the possibility to become just as complicated as current electronics, two very basic demonstrations will be shown below before discussing a more complex application in Chapter 4.

3.3.1 Flexible Electrodes

The first application is quite simple and entails the use of inkjet-printed carbon nanotube electrodes to turn ON a light emitting diode (LED). Figure 3.7 demonstrates this application. When the anode of power supply is not touching the carbon nanotube

network as shown in Figure 3.7(a), there is an open circuit, and the LED remains OFF. However, when the anode of the power supply is touching the carbon nanotube network as shown in Figure 3.7(b), current flows, and the LED turns ON.



(a) (b)

Figure 3.7 Inkjet-printed carbon nanotubes as flexible electrodes: (a) LED is OFF due to open circuit and (b) LED is ON due to closed circuit. The power supply was set to 5 V.

3.3.2 Inkjet-Printed Circuit Board

Many modern devices that claim flexibility are not entirely flexible. Rather, such devices make use of simple flexible components like ribbon cables. In addition to the possibility for a truly flexible circuit board where all of the components are completely flexible, there is yet another advantage of this technology. The term printed circuit board, or PCB for short, is a bit of a misnomer. To be clear, none of the steps for producing a PCB makes use of any type of printing. The technology presented in this thesis, however, would allow for the fabrication of truly *printed* circuit boards. As an

extension to the previous application, Figure 3.8 demonstrates a possible layout for an inkjet-printed circuit board (InkjetPCB) using carbon nanotubes.

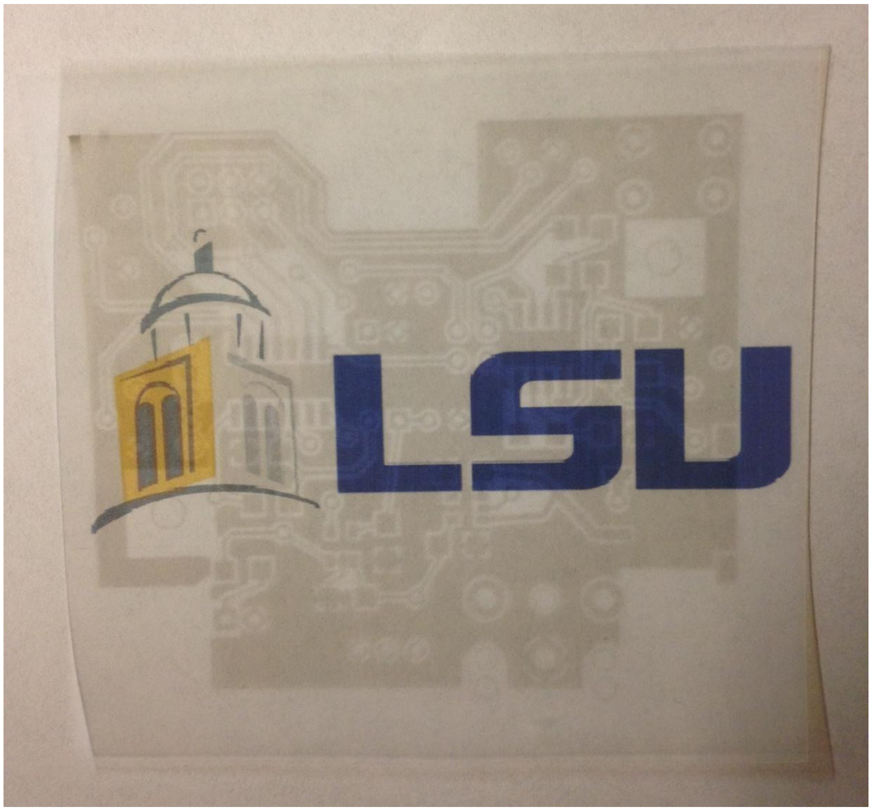


Figure 3.8 InkjetPCB fabricated using carbon nanotube inkjet printing on a transparency film.

3.4 Conclusion

Within this chapter, the process for preparing, printing, and optimizing carbon nanotube ink was reviewed. To the author's knowledge, this is the first reporting of carbon nanotube ink optimization for inkjet printing. In particular, suitable ranges of SDS:CNT ratios were found for both inks. For the SWCNT case, the optimum ratios range from approximately 5:1 to 10:1, and for the MWCNT case, the optimum ratios range from approximately 0.3:1 to 1.5:1.

Additionally, both the transparency and sheet resistance of the inkjet-printed carbon nanotube films were discussed in detail. Both the SWCNT ink and the MWCNT ink produced very conductive patterns, reaching as low as 132 Ω/☐ for SWCNTs and 286 Ω/☐ for MWCNTs. Again, in comparison to the reported sheet resistance data in Table 2.1, these sheet resistance values are among the lowest ever achieved for carbon nanotube inkjet printing.

As demonstrated throughout this chapter, there are an incredible amount of factors that can affect the properties of carbon nanotube ink. First and foremost, the carbon nanotube themselves play a major roll in the conductivity of the printed film. As discussed in Section 2.1, many carbon nanotube variations exist. Length, purity, and carbon nanotube type (i.e. conducting or semiconducting) are among the few properties of carbon nanotubes that affect the network conductivity.

Furthermore, only one dispersant was used in the carbon nanotube inks presented in this chapter. It would be very beneficial to investigate the use of other surfactants or polymers as dispersants in order to determine which dispersant yields the largest number of dispersed carbon nanotubes per unit volume. Although a more detailed comparison is necessary, the results presented in this chapter are truly quite noteworthy.

4. INKJET-PRINTED CARBON NANOTUBE ELECTRODES FOR ELECTROCHEMICAL CELL APPLICATIONS[2]

Considering the limited number of reports on carbon nanotube inkjet printing, few applications have been demonstrated. As one would expect, highly conductive carbon nanotube electrodes would prove to be very useful for many applications. Thus, as a simple but certainly novel demonstration, this chapter presents a fully printed electrochemical cell with carbon nanotube electrodes. Although inkjet-printed carbon nanotubes have been previously characterized using cyclic voltammetry (CV) [57], to the author’s knowledge, the demonstration of such electrodes for the electrochemical detection of chemical species has not been reported thus far.

4.1 Introduction

An electrochemical detection of species offers many advantages in chemical sensing including high sensitivity and selectivity. Moreover, its benefits of being low cost, simple, and easily miniaturized have a competitive edge over other sensing methods such as spectroscopy or chromatography, which can be quite expensive and bulky. Finally, the use of nanoparticles and nanowires can greatly improve the sensing performance in terms of lowering the detection limit and improving the sensor’s specificity [67]. This chapter presents a three-electrode electrochemical cell consisting

[2] This chapter previously appeared as R. P. Tortorich, E. Song, and J.-W. Choi, “Inkjet-printed carbon nanotube electrodes with low sheet resistance for electrochemical sensor applications,” *J. Electrochem. Soc.*, vol. 161, no. 2, pp. B3044-B3048, Jan. 2014. It is reproduced by permission of ECS — The Electrochemical Society [66].

of inkjet-printed carbon nanotube working and counter electrodes and a screen-printed silver/silver chloride (Ag/AgCl) reference electrode.

4.1.1 Sensor Fabrication

The sensor fabrication process is remarkably simple and low cost as illustrated in Figure 4.1. Patterns can be designed and adjusted through the use of computer-aided design (CAD) software with absolutely no time or money consumed by template fabrication or post-deposition patterning. Thus, inkjet-printed carbon nanotube electrodes have great potential for being used in a low cost, mass producible, and miniaturized electrochemical sensor with high performance. In performing cyclic voltammetry on the device, the feasibility of inkjet-printed carbon nanotube electrodes for use in an electrochemical sensor is demonstrated.

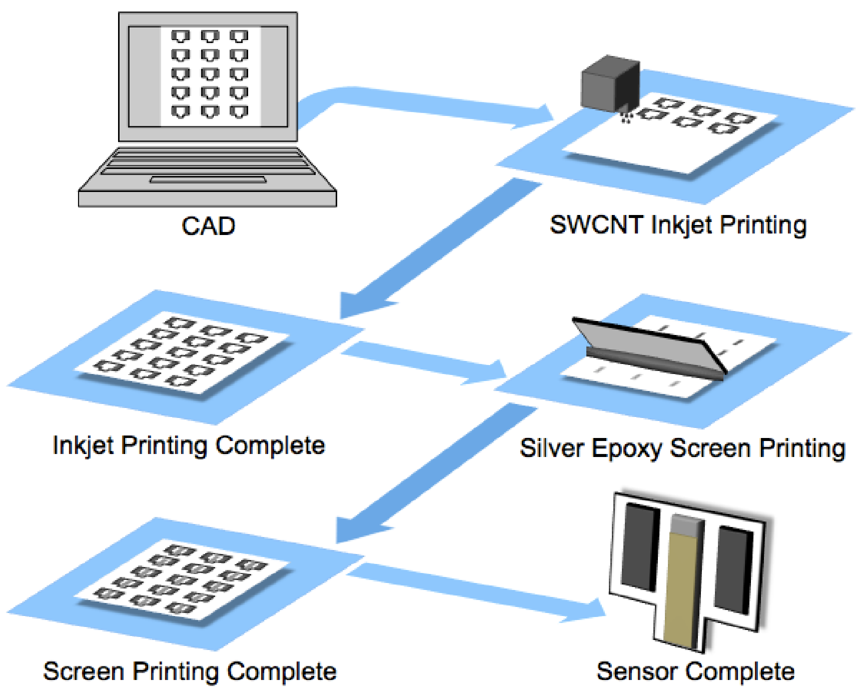


Figure 4.1 Schematic illustration of the fully printed sensor fabrication process.

4.2 Experimental Methods

Before presenting the results of this application, the experimental methods will be discussed in detail. Both ink preparation and sensor testing procedures are specified. Please note that the same ink-development process as discussed in Chapter 3 was followed for this demonstration. However, a brief summary is provided for convenience.

4.2.1 Carbon Nanotube Ink Preparation

Briefly, an aqueous solution containing 0.8 mg/ml of SWCNTs and 3 mg/ml of SDS was prepared and sonicated for 30 minutes. After sonication, the carbon nanotube ink was centrifuged at 12,000 rpm for 5 minutes and the supernatant was removed. Next, the contact angle of the supernatant was measured to ensure that the surface tension was low enough for consistent printing. Finally, the supernatant was injected into a clean ink cartridge (HP 56) and printed using an HP Deskjet 5650 inkjet printer.

To deposit the highest number of SWCNTs, the printer settings were adjusted for the best print quality, which ejected the largest volume of ink onto the substrate. Patterns for inkjet printing were quickly and easily designed in Microsoft Word or PowerPoint. The SWCNT ink was printed multiple times on the same area in order to achieve the lowest sheet resistance.

4.2.2 Electrochemical Sensor Testing Procedure

For cyclic voltammetry measurement, an area of approximately 2.5 mm x 5 mm of the printed electrodes was immersed in an electrolyte solution containing various amounts of $FeSO_4$ in 0.1 M H_2SO_4. A simple potentiostat circuit was built in order to

control the working electrode potential with respect to the Ag/AgCl reference electrode. The reference electrode was made by first screen printing a silver epoxy electrode on the transparency film. Then, a layer of AgCl was deposited by applying an anodic current of 0.2 mA for 90 minutes while immersing the film in a 1 M potassium chloride (KCl) solution. For comparison, gold electrodes were used as both working and counter electrodes in a separate electrochemical cell. A LabView FieldPoint module was used for the voltage control and current measurement. The current flowing out of the working electrode and into the solution (anodic current) was taken as a positive value for current measurement.

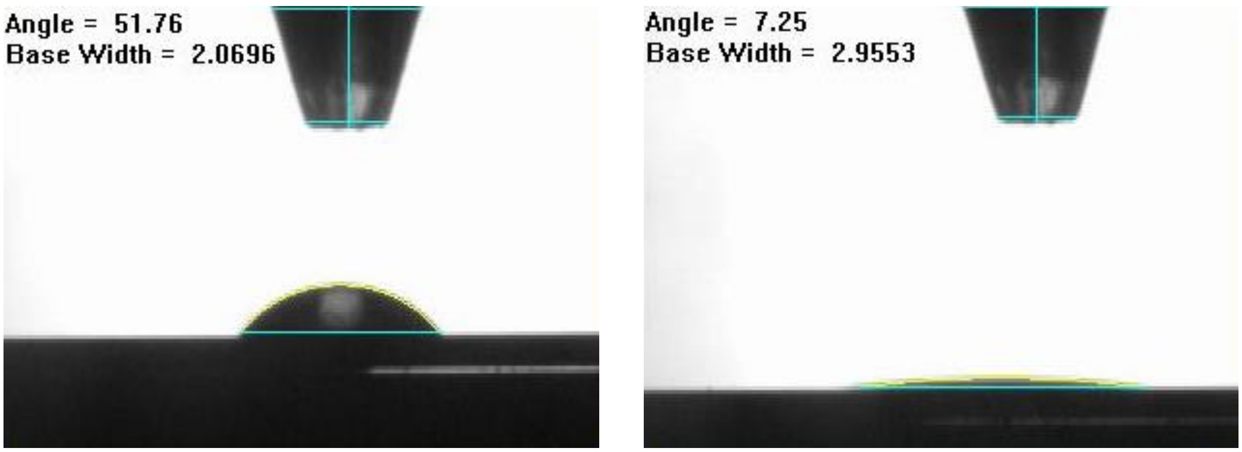
4.3 Results and Discussion

In order to obtain the maximum conductivity, highly concentrated carbon nanotube ink was used. This ensured that, with each print layer, a large volume of carbon nanotubes was deposited onto the substrate. After discussing the carbon nanotube sheet resistance results, the cyclic voltammetry results will be presented and discussed in detail.

4.3.1 Carbon Nanotube Sheet Resistance

Due to the use of a highly concentrated carbon nanotube ink, even with a single print, a sheet resistance as low as 7.4 kΩ/□ was achieved. To the author's knowledge, this is the lowest sheet resistance ever reported for a single layer of carbon nanotubes produced by inkjet printing. As mentioned in Section 3.1, such a high concentration of nanotubes would likely not be possible with the use of either functionalization or organic

solvents. Although functionalization is capable of preventing flocculation of carbon nanotubes, dispersants are far more effective at high concentrations. Figures 4.2(a) and 4.2(b) show images of the contact angle measurements for the SWCNT ink as well as deionized water for a comparison.



(a) (b)

Figure 4.2 Carbon nanotube ink contact angle measurement: (a) optical image showing high surface tension of water (volume: 2 μl, contact angle: 51.76°) and (b) optical image showing low surface tension of SWCNT ink (volume: 2 μl, contact angle: 7.25°). An untreated bare silicon wafer was used as the substrate for both contact angle measurements.

In order to achieve a low sheet resistance with the prepared carbon nanotube ink, multiple prints were performed, allowing for a highly dense network of carbon nanotubes to form. As discussed in Section 2.3.3, with each subsequent print, the carbon nanotube film became less and less transparent. Figure 4.3 shows an image of the SWCNT ink printed onto a transparency film 1-5 times as well as a scanning electron microscope (SEM) image of printed SWCNTs.

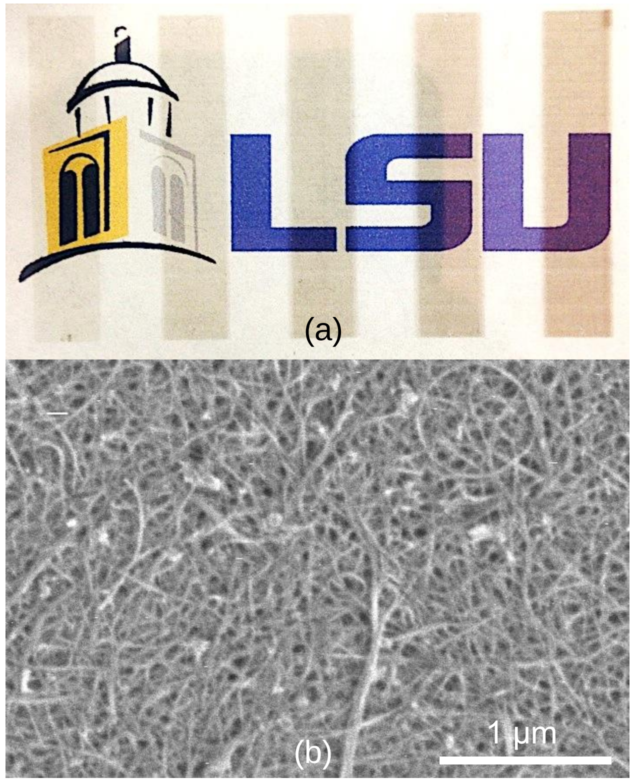


Figure 4.3 Inkjet-printed carbon nanotube electrodes: (a) an optical image showing 1-5 prints of SWCNT ink on a transparency film and (b) an SEM image of a printed SWCNT electrode. The width and spacing of the patterns in (a) are 5 mm.

The SWCNT ink was printed up to 35 times, reaching a sheet resistance as low as 132 Ω/☐. This is an extremely low sheet resistance for inkjet-printed carbon nanotubes, second only to 78 Ω/☐ (200 prints) demonstrated by Chen *at al* [57]. It should also be noted that there does not seem to be any degradation in conductivity of the printed film over an extended period of time provided the surface is not scratched or damaged. After obtaining a low sheet resistance, the electrochemical sensor was fabricated on a transparency film by carbon nanotube inkjet printing and silver epoxy screen printing. The completed device is shown in Figure 4.4.

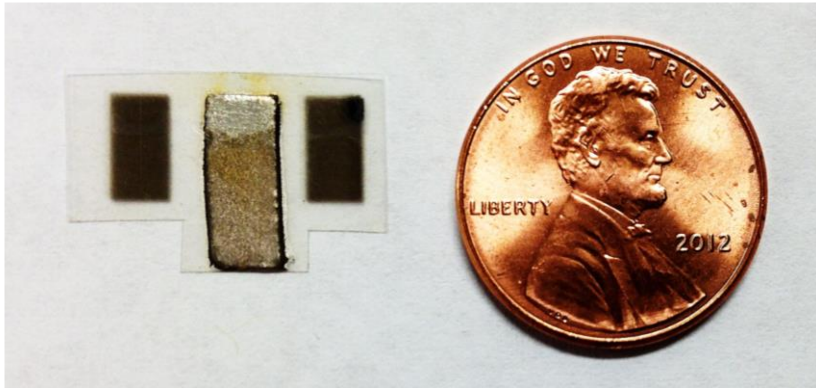


Figure 4.4 Optical image of the fully printed electrochemical sensor with inkjet-printed carbon nanotube working and counter electrodes and screen-printed Ag/AgCl reference electrode.

4.3.2 Cyclic Voltammetry

Following fabrication of the electrochemical sensor, cyclic voltammetry (CV) was performed in order to demonstrate the effectiveness of inkjet-printed carbon nanotubes as conducting electrodes. It should be noted that the carbon nanotubes seem to exhibit good adhesion to the transparency surface considering there was no visible contamination of the test solution with carbon nanotubes. Furthermore, upon measuring the film resistance after testing, there was no observable decrease from the original measurement. As a comparison, CV was performed first with gold electrodes and then with SWCNT electrodes. Figure 4.5 shows the CV curve for the redox reaction couple where the anodic peak indicates the conversion from Fe^{2+} to Fe^{3+} and the cathodic peak indicates the reverse reaction. Although the redox current peaks are clearly observed for the SWCNT-based electrodes, the potentials at which such peaks occur do not align well with respect to the conventional gold electrodes as depicted in Figure 4.5.

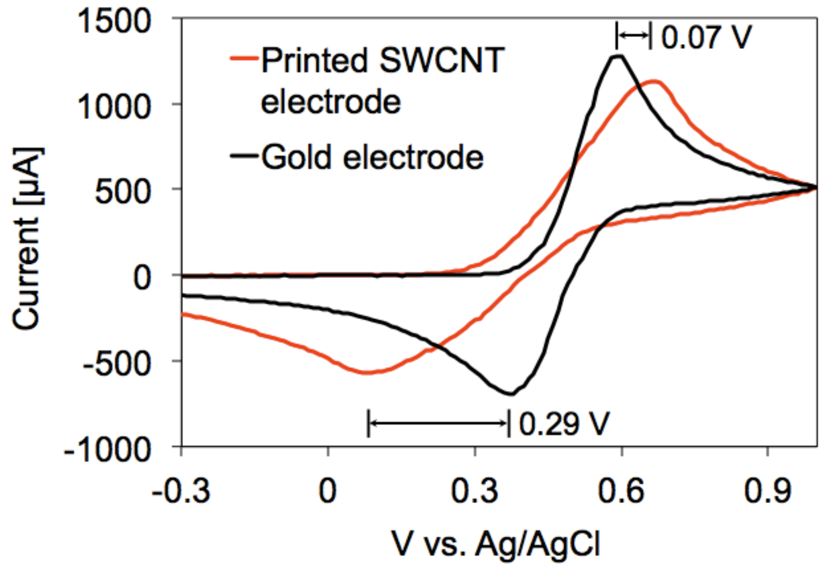


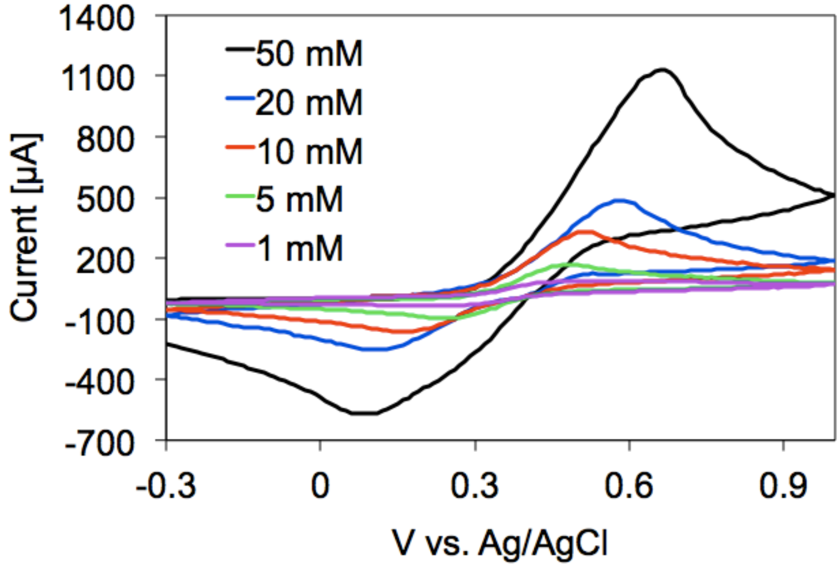
Figure 4.5 A comparison of the CV curves between the inkjet-printed SWCNT electrodes and the conventional gold electrodes. The electrode area was approximately 2.5 mm x 5 mm, and the scan rate for both electrodes was 50 mV/s. The potential shift in the anodic and the cathodic peak currents are also indicated in the figure.

This is due to the relatively large sheet resistance in the carbon nanotube network resulting in a significant voltage drop within the electrode. This can be confirmed by calculating the approximate voltage drop across the SWCNT electrode. For instance, with the sheet resistance of 132 Ω/☐for the SWCNT electrode, the anodic peak current of 1.13 mA occurring at +0.66 V creates a voltage drop of 0.15 V per unit square of the electrode. Since only a half of the square area was immersed in the solution, an estimated voltage drop of 0.075 V across the immersed electrode can be expected. This number is in close agreement with the anodic peak shift between the gold and the SWCNT electrodes. On the other hand, the shift in the cathodic peak is larger than the anodic shift due to the irreversibility of the electrochemical reaction.

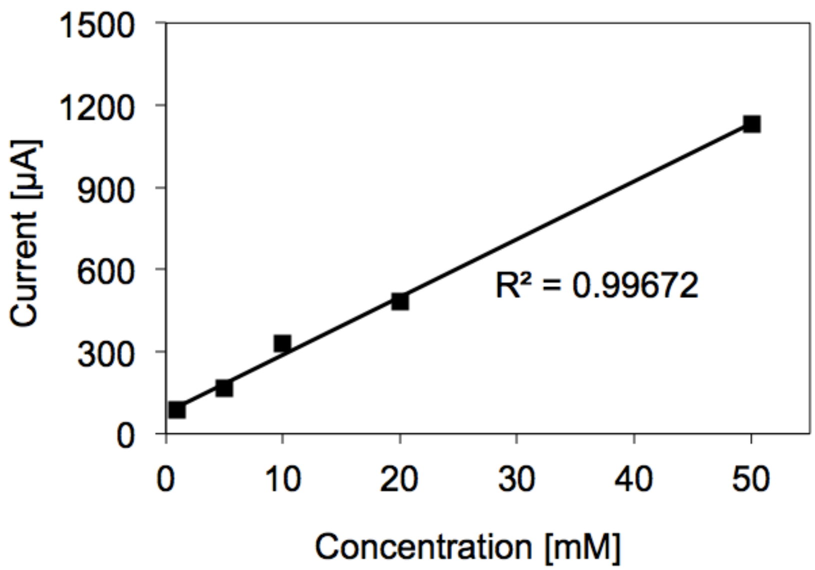
Figure 4.6(a) shows a set of CV curves obtained using the fully printed electrochemical sensor with various concentrations of $FeSO_4$ in the solution. More

specifically, these experimental results demonstrate a reliable electrochemical measurement for the detection of iron ions with concentrations ranging from 1 mM to 50 mM. Figure 4.6(b) shows a calibration curve plotting the peak anodic currents for various concentrations as obtain in Figure 4.6(a). This curve shows that the peak anodic current value can be used to accurately determine the iron concentration in the sample solution. As indicated by the R^2 value of the trend line, the peak response is highly linear with respect to the analyte concentrations. With the current electrochemical setup, the detection limit for the iron sensor is approximately 1 mM. However, the limit of detection for the printed SWCNT electrode-based sensor could be lowered with optimized electrochemical techniques. Miniaturization of the printed electrodes can also help to improve the sensing performance.

In addition to the DC measurements, the impedance of the printed SWCNT patterns was measured using a frequency range from 20 Hz to 2 MHz. For this range, no phase change was observed, suggesting that the carbon nanotube electrodes behave as ohmic conductors for frequencies up to 2 MHz, which is sufficient for this demonstration. However, for high frequency applications, further characterization of the carbon nanotube electrodes is necessary.



(a)



(b)

Figure 4.6 Electrochemical response of the inkjet-printed SWCNT electrodes with different concentrations of iron in the electrolyte solution: (a) a set of CV plots with iron concentrations ranging from 1 mM to 50 mM and (b) a calibration curve showing the peak anodic current values versus the iron concentration. The potential scan rate was 50 mV/s.

4.4 Conclusion

In this chapter, the methods for preparing and printing carbon nanotube ink were reviewed and the relevant sheet resistance measurements were given. Although the lowest sheet resistance of 132 Ω/☐does result in a shift in the CV curve, it is still one of the lowest sheet resistances ever reported for inkjet printing of carbon nanotubes. In addition to the demonstration of inkjet-printed carbon nanotubes, the use of these printed carbon nanotubes as electrodes in an electrochemical sensor was demonstrated. The CV curves confirm that it is indeed feasible to use inkjet-printed carbon nanotube as electrodes in an electrochemical ionic sensor.

In combining both inkjet printing and carbon nanotubes, it is possible to easily fabricate cheap, flexible, and disposable electrochemical sensors. With further optimization of the SWCNT ink, a lower limit of detection may be possible since carbon nanotubes offer a very high surface area. Aside from this simple demonstration, the advantages of both carbon nanotubes and inkjet printing lend themselves to a vast number of applications especially in the field of biological and chemical sensing.

5. SUMMARY AND CONCLUSIONS

Throughout this work, two very promising technologies were merged in order to provide a foundation for a new branch of electronics and sensors. In particular, inkjet printing was used to deposit carbon nanotubes onto a flexible substrate for use as flexible electrodes. The process for preparing, printing, and optimizing carbon nanotube ink was reviewed in detail. Along the way, comparisons were made between single-walled carbon nanotube (SWCNT) ink and multi-walled carbon nanotube (MWCNT) ink. Again, although these comparisons are not ideal, the information provided serves as a basis for further investigation. Additionally, multiple applications for inkjet-printed carbon nanotube electrodes were demonstrated.

5.1 Research Goals

In Chapter 1, four research goals were provided. Each one will be briefly reviewed in order to determine the extent to which each goal was accomplished.

The first goal was to develop conductive SWCNT ink and MWCNT ink for inkjet printing. As demonstrated by the sheet resistance curves, both the SWCNT ink and the MWCNT ink were very conductive. However, considering the large number of factors that affect the CNT network conductivity (length, purity, type, etc.), it is likely that the conductivity can be increased with further research.

The second goal was to optimize the SWCNT and MWCNT inks in order to obtain the lowest possible sheet resistance. As demonstrated by the optimization data, an optimum range of SDS:CNT ratios was determined for both inks. Of course, it is important to note that these optimum ratios are specific to the particular carbon

nanotubes used as well as the dispersant used. If other types of carbon nanotubes are used, the ratio may change. Likewise, if another dispersant aside from SDS is used, the ratio may change.

The third goal was to characterize the SWCNT and MWCNT inkjet-printed thin films. Here again, the goal was achieved, but further characterization is indeed possible. Both the sheet resistance and the transparency, which are the two primary characteristics of the CNT electrodes, were discussed in Chapter 3. Other possible characteristics to consider are thickness, resistance vs. curvature, and long-term stability.

The fourth goal was to fabricate and characterize a fully printed electrochemical sensor that uses inkjet-printed CNT electrodes. As demonstrated in Chapter 4, the fabrication of a fully printed electrochemical sensor was achieved. The results of the cyclic voltammetry tests are very promising and confirm the possibility for the use of inkjet-printed carbon nanotubes as flexible electrodes.

5.2 Suggestions and Future Work

As with any type of research and development process, there is always further work to be done. Of course, one could devote a tremendous amount of time to any particular aspect of carbon nanotube inkjet printing, but there are a few practical investigations worth noting.

In Chapter 3, it was observed that for SDS concentrations much higher than the CMC, the carbon nanotube films were more transparent and thus less conductive. Again, this is likely due to an increased number of micelles being formed within the

solution. One possible experiment for confirming this hypothesis is quite simple. In the current process of preparing carbon nanotube ink, all of the SDS is placed in the bottle prior to sonication. In order to mitigate micelle formation, small amounts of SDS could be added periodically. For example, in preparing an ink with 8 mg/ml of SDS, only half of the SDS (4 mg/ml) would be placed in the bottle prior to sonication. Then, after a 30 minute sonication period, the other half of the SDS (4 mg/ml) would be added, followed by another 30 minute sonication period. This process would ensure that the dispersant molecules do indeed contribute to the carbon nanotube dispersion rather than form individual micelles. As a result, a better dispersion (i.e. more carbon nanotubes per unit volume) could be achieved and thus a lower sheet resistance.

In addition to investigating the role of SDS, it would be very beneficial to confirm the consistency of the optimization data. As mentioned previously, the optimization data should maintain the same general shape with varying carbon nanotube concentrations, provided the SDS:CNT ratios are maintained. To confirm this, both a higher (1.0 mg/ml) and a lower (0.6 mg/ml) SWCNT concentration could be used. The same process could be done for the MWCNT case as well.

Aside from these two simple suggestions, this work has incredible potential. As mentioned in Section 1.2, nearly any electronic device can be made using three specific material categories: conductors, semiconductors, and dielectrics. Although the focus of this thesis was inkjet printing of carbon nanotubes, virtually any kind of nanomaterial can be printed with an inkjet printer, provided the ink maintains a good dispersion as well as both low surface tension and viscosity. Thus, fully inkjet-printed devices can be realized. As an example, with the development of a silver nanowire ink, the

electrochemical sensor presented in Chapter 4 could be fabricated entirely with an inkjet printer. Additionally, since carbon nanotubes themselves can either be conducting or semiconducting, the fabrication of semiconductor devices like transistors is indeed possible. On the other hand, semiconducting nanowires like silicon could be used as well. As with current electronic devices, virtually anything is possible. Of course, this concept is certainly in its early stages and will require time to develop, but the information presented in this work lays a solid foundation for future research regarding the fabrication of flexible electronics and sensors using inkjet printing.

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Ryan Tortorich was born and raised in New Orleans, Louisiana. He graduated as salutatorian from Archbishop Rummel High School in May 2008 and entered Louisiana State University in August 2008. After receiving his Bachelor of Science in Electrical Engineering in May 2012, he pursued a graduate degree in the Department of Electrical and Computer Engineering at Louisiana State University. In May 2014, he is a candidate for his Master of Science in Electrical Engineering.