Printing Nanotube/Nanowire for Flexible Microsystems

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ABSTRACT

Printing has become an emerging manufacturing technology for mechanics, electronics, and consumer products. Additionally, both nanotubes and nanowires have recently been used as materials for sensors and electrodes due to their unique electrical and mechanical properties. Printed electrodes and conductive traces particularly offer versatility of fabricating low-cost, disposable, and flexible electrical devices and microsystems. While various printing methods such as screen printing have been conventional methods for printing conductive traces and electrodes, inkjet printing has recently attracted great attention due to its unique advantages including no template requirement, rapid printing at low cost, on-demand printing capability, and precise control of the printed material. Computer generated conductive traces or electrode patterns can simply be printed on a thin film substrate with proper conductive ink consisting of nanotubes or nanowires. However, in order to develop nanotube or nanowire ink, there are a few challenges that need to be addressed. The most difficult obstacle to overcome is that of nanotube/nanowire dispersion within a solution. Other challenges include adjusting surface tension and controlling viscosity of the ink as well as treating the surface of the printing substrate. In an attempt to pave the way for nanomaterial inkjet printing, we present a method for preparing carbon nanotube ink as well as its printing technique. A fully printed electrochemical sensor using inkjet-printed carbon nanotube electrodes is also demonstrated as an example of the possibilities for this technology.

Keywords: inkjet printing; carbon nanotube printing; carbon nanotube ink; flexible electronics; printable electronics

1. INTRODUCTION

Nanotechnology has become a well-established field of study in recent years. Various nanomaterials are being used in spectacular ways in order to further enhance nearly any kind device or product. In particular, both nanotubes and nanowires have been used in numerous applications including mechanical, electrical, chemical, and even biological applications. Although the use of nanomaterials involves a number of issues and considerations, the deposition method for such materials is indeed one of great importance. Multiple forms of nanomaterial deposition exist including electrophoretic deposition[1–3], dip coating[4], spray coating[5–8], and others. In addition to these methods of deposition, various forms of printing have been used for nanomaterial deposition, allowing for low-cost fabrication of disposable and flexible electrical devices and microsystems. Some of the printing methods used for nanomaterial deposition include aerosol printing[9–11], screen printing[12], contact printing[13], and transfer printing[14], but the most useful and effective method of printing is inkjet printing. Unlike other methods of printing, inkjet printing does not require templates in order to produce patterns on a substrate, which reduces manufacturing cost. Additionally, inkjet printing allows for faster device fabrication due to its on-demand printing capability. Finally, with inkjet printing, multiple materials can be deposited during the same fabrication step and with precise control of the material thickness.

The motivations for using inkjet printing as a deposition method are numerous, but the true significance of this technology lies in its potential applications. Unlike other types of fabrication and deposition, inkjet printing allows for the development of flexible microsystems. Such microsystems could be used within either flexible electronics or flexible sensors. In terms of specific applications, flexible microsystems could have a significant impact in the biomedical field, allowing for small and durable devices within the human body as well as wearable electronics and sensors that contour to the skin. Figure 1 illustrates the general process for using inkjet printing as a means to fabricate flexible microsystems.

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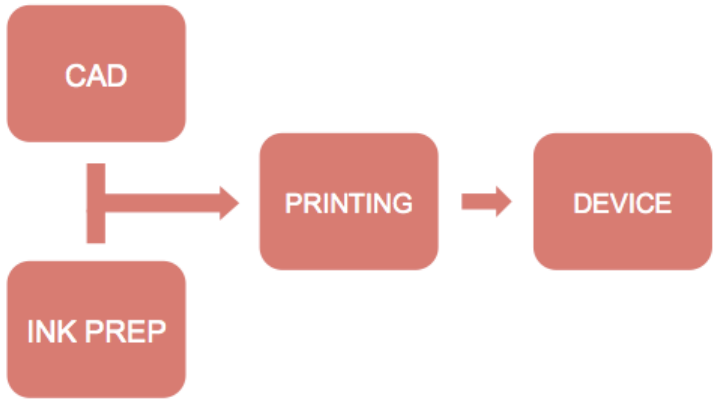

Figure 1: Block diagram of inkjet printing process for device fabrication.

2. INK PREPARATION AND PRINTING

The development of nanotube/nanowire ink for inkjet printing requires knowledge of the inkjet printing process. The nozzle of an inkjet cartridge contains numerous holes through which tiny droplets of ink are ejected. In order for the nanotube/nanowire ink to be ejected properly, three properties must be met. First, the nanotubes/nanowires must be dispersed properly in order to prevent flocculation, which could clog the nozzle. Additionally, the nanotube/nanowire ink must maintain both low surface tension and viscosity.

2.1 Carbon Nanotube Dispersion

In order to demonstrate the ability of inkjet printing to be used for fabrication of flexible microsystems, we first developed a carbon nanotube (CNT) ink. In particular, we developed both a single-walled carbon nanotube (SWCNT) ink and a multi-walled carbon nanotube (MWCNT) ink. Our previous publication offers a detailed review of carbon nanotube inkjet printing and its current progress[15]. Briefly, dispersion of carbon nanotubes within a solution can be achieved in multiple ways. Although the concentration limit is low, carbon nanotubes can be dispersed within organic solvents such as dimethylformamide (DMF)[16–21] and N-methyl-2-pyrollidone (NMP)[22] without the use of other materials. On the other hand, aqueous dispersions of carbon nanotubes are only possible through the use of sidewall functionalization[23–25] or the addition of other dispersants[26–30] such as polymers and surfactants.

2.2 Carbon Nanotube Ink Preparation

We decided to avoid using organic solvent-based carbon nanotube ink due to their volatile and sometimes corrosive nature. As a result, we developed a water-based carbon nanotube ink using sodium n-dodecyl sulfate (SDS) as the dispersant. SDS is a surfactant that adheres to the carbon nanotube surface due to a hydrophobic interaction. Fortunately, the SDS also works to reduce the surface tension of the water-based ink, which is crucial for uniform and continuous inkjet printing. To prepare the carbon nanotube ink, the appropriate amount of carbon nanotubes and SDS were measured and placed in a glass bottle. The glass bottle was then sonicated for 30 minutes using a bath sonicator (FS20D, Fisher Scientific). Following sonication, the carbon nanotube ink was centrifuged at 12,000 rpm for 5 minutes, and the supernatant was removed. This ensures that large clumps of carbon nanotubes are removed from the solution prior to printing, which is necessary to prevent clogging of the nozzle. Next, the contact angle of the ink was measured (FTA125, First Ten Angstroms). This was done in order to verify that the surface tension of the ink was low enough for printing. Typically, contact angles below 20° allowed for continuous and uniform printing (volume: 2 µl, substrate: silicon wafer). Finally, the ink was injected into a clean ink cartridge (HP 56) and printed using an HP Deskjet 5650 inkjet printer. Primary substrates used during printing were paper and transparencies.

2.3 Carbon Nanotube Printing

After achieving a printable and stable carbon nanotube ink, optimization was necessary in order to reduce the film sheet resistance, which is ideal for using printed carbon nanotubes as flexible electrodes. We suspected that varying the

SDS:CNT ratio would play a major role in determining the sheet resistance of the printed carbon nanotube film. As a result, we varied this ratio and measured the sheet resistance using a standard two-point probe ohmmeter. Figure 2 shows an optimization curve for various SDS:MWCNT ratios.

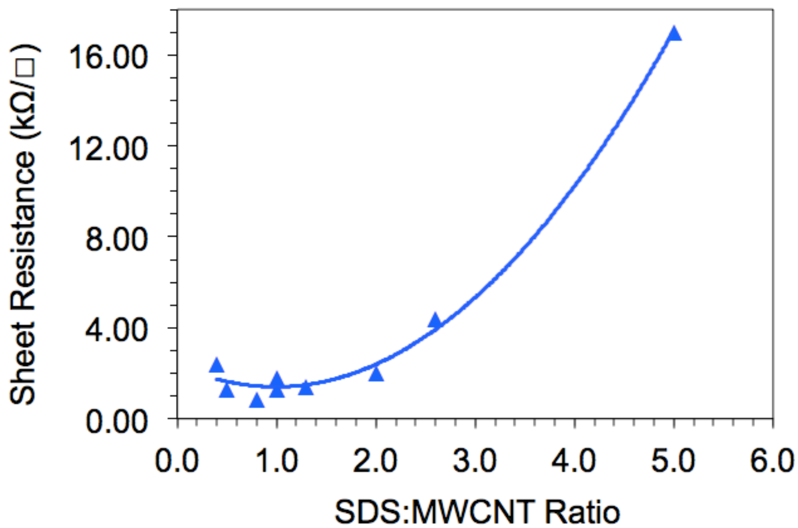

Figure 2: SDS:MWCNT ratio optimization curve. Sheet resistance was measured after five prints of each ink composition on a transparency film.

As illustrated in Figure 2, there seems to be an optimum ratio of approximately 0.8. For ratios above this value, more SDS molecules cover the carbon nanotube surface, preventing direct contact between carbon nanotubes and thus increasing the resistance of the film. On the other hand, for ratios below this value, there are not enough SDS molecules covering the carbon nanotube surface, allowing flocculation of carbon nanotubes. This in turn reduces the overall concentration of carbon nanotubes following the centrifuge step, which of course increases the resistance of the film.

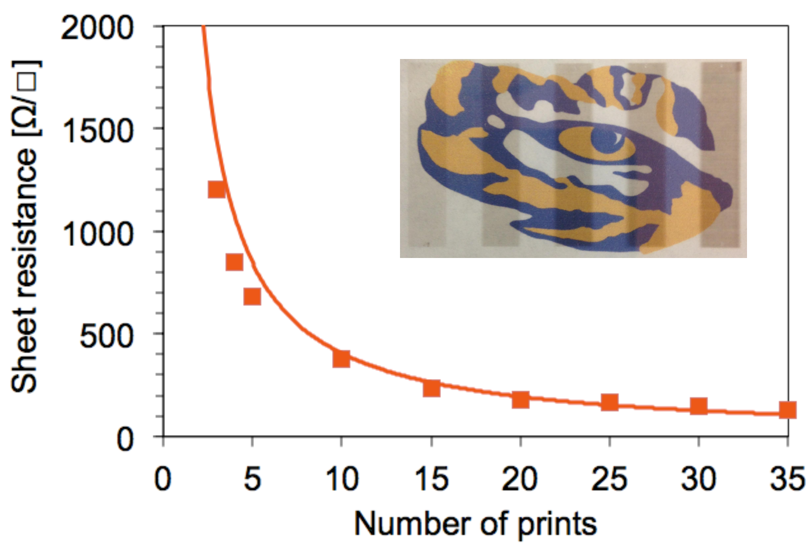

Figure 3: Measured sheet resistance of SWCNT ink. The SWCNT ink contains 0.8 mg/ml of SWCNTs and 3 mg/ml of SDS. Inset: optical image showing 1-5 prints of SWCNT ink on a transparency film.

In addition to optimizing the carbon nanotube ink, we also investigated the relationship between print number and sheet resistance. As expected, following each print, the sheet resistance decreases because more electron pathways are being created. Initially, there is an exponential decay in sheet resistance. However, eventually, the sheet resistance levels off and approaches the bulk conductivity. Additionally, with each subsequent print, the film becomes less transparent due to the addition of more and more carbon nanotubes. Figure 3 shows a sheet resistance curve for printed SWCNT ink along with an image of SWCNT electrodes.

As shown in Figure 3, we were able to achieve a low sheet resistance of 132 Ω/□. This is one of the lowest values ever reported for carbon nanotube inkjet printing. Additionally, Figure 3 shows that the SWCNT electrodes are transparent. However, it should be noted that with each subsequent print, the transparency decreases. Due to the low resistance and transparency, inkjet-printed SWCNT could potentially be used as transparent electrodes, possibly replacing the more expensive indium tin oxide (ITO).

3. PRINTED SENSOR TECHNOLOGIES

In order to demonstrate the use of carbon nanotube inkjet printing as a means to fabricate flexible electrodes, we developed a fully printed electrochemical sensor. Our previous publication presents a detailed description of this endeavor, but a brief overview will be provided[31]. Both the working electrode and the counter electrode were fabricated using carbon nanotube inkjet printing, while the reference electrode was fabricated using silver epoxy screen printing. Figure 4 shows a schematic illustration of the fabrication process.

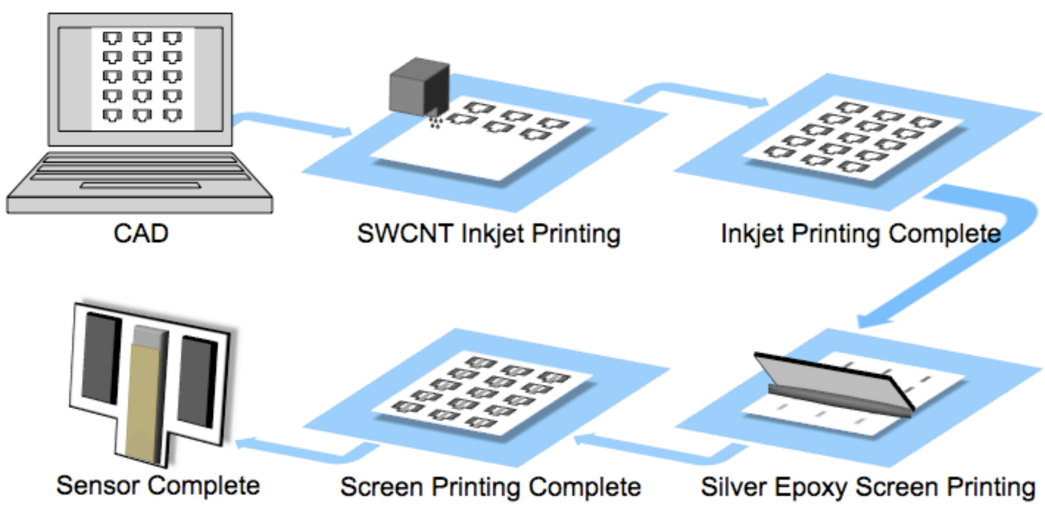

Figure 4: Schematic illustration of the inkjet printing process for fabricating an electrochemical cell on a flexible polymer substrate.

After fabricating the electrochemical sensor, cyclic voltammetry (CV) was performed in order to demonstrate its effectiveness. Using a simple potentiostat circuit along with a LabView FieldPoint module, we were able to control the potential of the working electrode with respect to the reference electrode and measure the resulting current. The current flowing out of the working electrode and into the solution (anodic current) was taken as a positive value for current measurement. Figure 5 shows the CV curve for the redox reaction where the anodic peak indicates the conversion from Fe^{2+} to Fe^{3+} and the cathodic peak indicates the reverse reaction.

After verifying the fully printed device was effective as an electrochemical sensor, it was necessary to determine its accuracy in measuring analyte concentration. This was done by simply performing CV using various analyte concentrations. The peak current was then plotted in order to obtain the calibration curve shown in Figure 6. The R^2 value indicates that the sensor is highly linear, which is a very desirable characteristic.

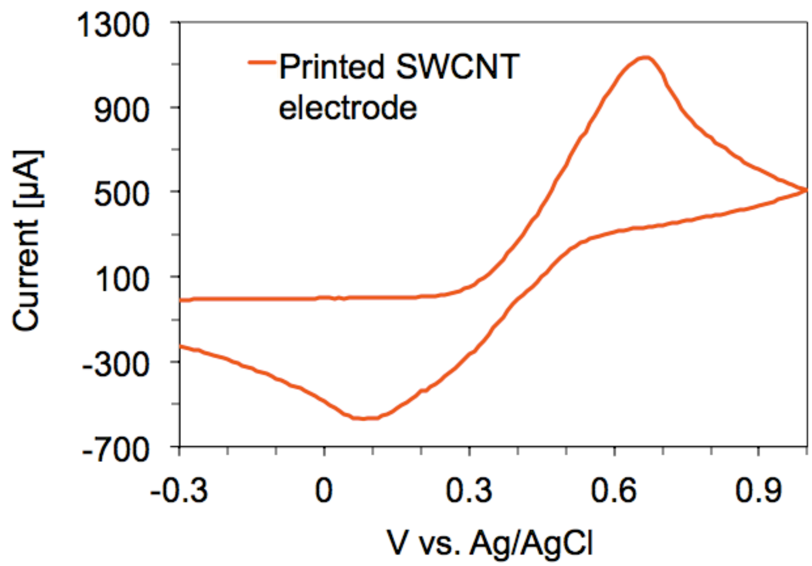

Figure 5: CV curve for the fully printed electrochemical sensor. The electrode area was approximately 2.5 mm x 5 mm, and the scan rate for both electrodes was 50 mV/s.

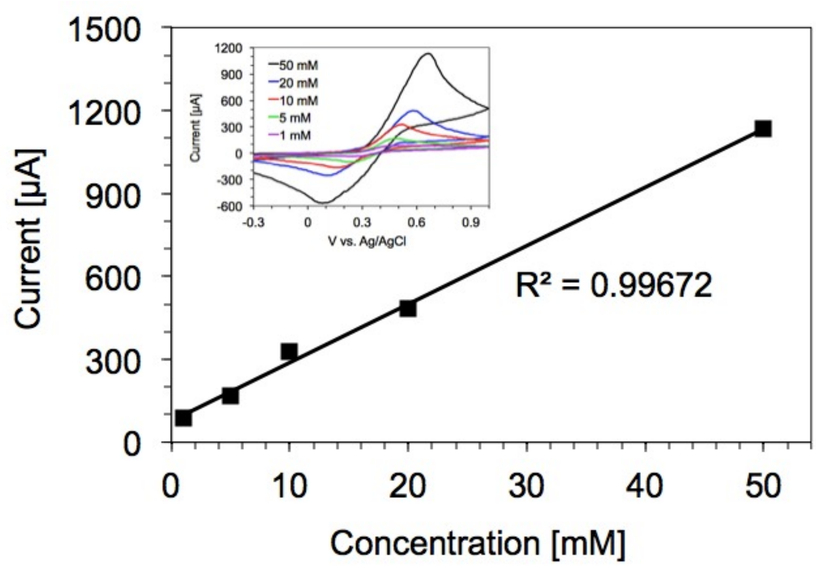

Figure 6: Calibration curve showing the peak anodic current values verses the iron concentration. Inset: set of CV plots with varying concentrations ranging from 1 mM to 50 mM and a scan rate of 50 mV/s.

4. CONCLUSIONS AND PROSPECTS

As discussed in this manuscript, nanotube/nanowire printing has great potential for use in flexible microsystems. Although we have demonstrated the use of carbon nanotubes for flexible conductive electrodes, other materials can be used in order to develop different types of ink with varying properties. For example, a silicon nanowire ink might be used as the semiconducting material for solid state devices such as field effect transistors. Furthermore, the combination of both carbon nanotubes and inkjet printing may allow for the fabrication of a multitude of chemical and biological sensors that are cheap, flexible, and disposable. Since the surface of carbon nanotubes can be functionalized, a series of chemical processes can be used so as to introduce selectivity to the carbon nanotubes. These sensors could then be incorporated into various diagnostic chips or wearable devices. The possibilities are truly astonishing, and it is safe to assume that the future of nanomaterial printing will have a significant impact on how electronic devices are used.

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