The E-jet printing of organic inks on organic substrates

Pei Lun Lai

Iowa State University

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The E-jet printing of organic inks on organic substrates

by

Pei Lun Lai

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee:
Reza Montazami, Major Professor
Nicole Nastaran Hashemi
ChunHui Xiang

The student author, whose presentation of the scholarship herein was approved by the program of committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2021

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ABSTRACT

Polyimide (PI) and Polydimethylsiloxane (PDMS) are substrates known for the fabrication of flexible electronics due to their mechanical properties. Herein, we utilized an additive manufacturing technique called electrohydrodynamic (e-jet) printing to deposit ink on top of the substrates. The E-jet printing process is a low-cost, high-resolution micro to a nanoscale printing system that fabricates flexible substrate patterns.

We presented an expansible exfoliation method to produce high-quality few-layer graphene (FLG) in the present work. Characterizations such as Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), and Raman were tested on the graphene samples. Experimental results showed that the graphene had a thickness of $7.6 \pm 2.3$ nm, suggesting the presence of single-layer to few-layers graphene sheets. Also, there were no cracks or defects spotted on the graphene nanosheets. The maximum lateral dimension of hundreds nm proved that the exfoliation of graphite to graphene was indeed successful. Then, the graphene was deposited on the substrate via the e-jet customize printer with a series of controlled parameters to ensure high resolution printed lines. The thermal annealing effect on printed lines was investigated, and we found out that the optimum temperature for our substrate is $280 \degree C$. We managed to drive down the sheet resistance of the printed lines from $138.75 \Omega/\text{sqr}$ to $41.75 \Omega/\text{sqr}$. 
Besides that, we also explored different substrates such as Polydimethylsiloxane (PDMS) due to its high stretchability and flexibility properties. Here, a highly stretchable graphene-PDMS was fabricated using the e-jet printing method. Experimental results showed that the substrate has demonstrated stretchability up to 30% and bending up to 27mm displacement. Also, the I-V curve illustrated a linear relationship between current and voltage, which suggested that the proposed sensor demonstrated ohmic resistor behaviors. The proposed sensor suggested that it can function normally in an environment temperature below 110 °C. Besides, we also indicated the stability of the proposed sensor under stretching and bending for 10 minutes, respectively. On the whole, the proposed sensor can be used in wearable electronic applications because of its high stretchability and flexibility.
CHAPTER 1. GENERAL INTRODUCTION

1.1 Flexible Electronics

Electronic components have been getting a lot of attraction in the last few years. One of the recent advancements is the Internet of Things (IoT), a network of exchanging and connecting data using a network protocol. The IoT builds upon mobile and network’s thorough success by enlarging the network of the network even further. From Fig 1.1, many smart surroundings can be involved in IoT infrastructure, such as smart health, smart home, smart transport, etc. There are numerous applications that can be used in these smart environments. For instance, smart production has consisted of applications such as smart production agriculture, smart production farming, and elegant production packaging. Also, the applications mentioned below are built based on one or a few technologies, including sensor, display, memory, RFID, etc.

Figure 1.1 Schematic diagram of the infrastructure of IoT, the related applications and the important key devices [1].
There are a few reasons why flexible electronics have the exact characteristics that are required for the IoT:

1) Materials like organic materials that are used in flexible electronics are relatively cheap.  
2) The manufacturing methods for flexible electronics are inexpensive, such as inkjet printing, electrohydrodynamic printing, etc.  
3) The devices fabricated are mechanically flexible because it is made of flexible organic materials and manufactured on substrates such as PI, PET, PDMS, etc.

1.2 Introduction to Graphene

Graphene is an exciting material. It is a single two-dimensional layer of sp$^2$ bonded carbon atoms closely packed arrangement in a honeycomb crystal lattice, as shown in Fig 1.2. It has gained tremendous attention due to its physical, mechanical, and electrical properties. Because of these unique properties, graphene can have an enormous impact in areas/fields like chemical sensors [2], supercapacitors [3], field-effect transistors [4], and light-emitting diodes [5]. Table 1.1 summarizes the characteristics of graphene and its value.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
<th>References</th>
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<tbody>
<tr>
<td>Surface area</td>
<td>2630 m$^2$g$^{-1}$</td>
<td>[6]</td>
</tr>
<tr>
<td>Intrinsic mobility</td>
<td>200000 cm$^2$v$^{-1}$s$^{-1}$</td>
<td>[7]</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>~1.0 TPa</td>
<td>[8]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>~5000 Wm$^{-1}$K$^{-1}$</td>
<td>[9]</td>
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1.3 Graphene Production Method

Until now, there are several methods of synthesizing graphene ink. However, each way presents different ink characteristics, properties, and flexibility of graphene. A few methods that the industry has used are described below:

1.3.1 Chemical Exfoliation like Hummers’ Method

Hummers’ method was developed in 1958 to be faster and more efficient in producing graphite oxide [11]. The reaction occurred between the graphene and the sulfuric acid with the sodium nitrate and potassium permanganate as the catalyst. Before that, Staudenmaier developed a method to synthesis graphite oxide from graphite by adding potassium chlorate as the oxidizing agent [12]. Unfortunately, this method did not go well because the oxidation step takes up to one week. One advantage of using Hummers’ method is producing graphene in large quantities in a shorter period (~2hr). However, the reduced material causes low electrical conductivity due to the bonding feature [13].

1.3.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a method that can produce high-quality graphene on a large scale by depositing it on transition metal substrates. The experimental setup is shown
in Figure 1.3. This method is inexpensive and works by feeding gas species into the reactor and pass through the hot zone; then, the hydrocarbon precursors decompose to carbon radicals and form single or few layers (FLG) graphene. Over the years, researchers have been exploring different kinds of transition metal substrates such as Cu [14], Re [15], Pt [16], and Ir [17]. For example, Ruoff et al. developed an attractive method to grow graphene directly on the surface of the copper film, and the film is mostly graphene, with less than 5% of the area having 2-to-3-layer graphene flakes [18].

![Figure 1.3 Schematic diagram of experimental setup for CVD process [17]](image_url)

1.3.3 Mechanical Exfoliation

Mechanical exfoliation mechanisms worked by overcoming the Van der Walls attraction between adjacent graphene flakes. There are a few mechanical exfoliation techniques, such as micromechanical cleavage, that the industry has used to produce graphene. However, this method possessed drawbacks in fulfilling the potential. For instance, micromechanical cleavage, a.k.a. the scotch tape method in Fig 1.4 can be used to produce few-layer or even single-layer high-quality graphene by pressing the tape against the surface of the graphite, but it is a shame that this method doesn’t meet the demand of producing graphene in bulk [19]. For the past few years, the ball milling technique has been getting a lot
of attention because it is able to produce excellent and quality graphene productions. The ball milling technique utilized shear force to exfoliate into graphene flakes. But there are still problems that need to be addressed, such as the size and type of the grinding media and the ability to accurately control the high energy collision to produce high-quality graphene.

Figure 1.4 Working procedure of micromechanical exfoliation process [20]

Table 1.2 Summary of the graphene production methods

<table>
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<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref</th>
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<td>Mechanical Exfoliation</td>
<td>- Produces high quality graphene</td>
<td>- Labour intensive and time consuming</td>
<td>[21]</td>
</tr>
<tr>
<td>Liquid Phase Exfoliation</td>
<td>- Solution processable</td>
<td>- Requires centrifugation to separate from dispersion liquid</td>
<td>[22]</td>
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<tr>
<td></td>
<td>- Low risk process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical Vapor Deposition</td>
<td>- Produces large area films transferable to other substrates</td>
<td>- High temperature</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Energy intensive process</td>
<td></td>
</tr>
<tr>
<td>Reduction of graphene oxide</td>
<td>- Solution processable</td>
<td>- Produces lower quality chemical modified graphene</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>- Low-risk process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epitaxial growth on SiC substrate</td>
<td>- Produces high quality films free from heteroatoms</td>
<td>- Difficult to transfer from SiC to different substrate for application</td>
<td>[25]</td>
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CHAPTER 2. THE E-JET PRINTING OF ORGANIC INKS ON ORGANIC SUBSTRATES

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A paper submitted to the *Journal of Biosensors*

2.1 Introduction

Over the past few years, it has been not surprising that flexible electronics has been the focal point of attraction because it has shown the capability to become the next technology innovation in electronics. In Fig 2.1, flexible electronics are often employed in different forms of applications ranging from flexible sensors such as biomedical devices [1], personal wearable devices [2], and solar cells [3]. The manufacturing process of flexible electronics is unique because it has a bigger overall dimension and can have different types of substrates. Many researchers are developing new fabrication methods to replace the traditional process of photolithography [4]. Despite having excellent reliability within the photolithography process, it doesn’t play a vital role in flexible substrate because it is not ideal for rapid modification and contains multiple processing steps, which increases the cost of fabrication.

![Fig 2.1 Schematic diagram of flexible electronics and their applications](image-url)

Fig 2.1 Schematic diagram of flexible electronics and their applications
In comparison, additive manufacturing processes showed their potential to be the following big thing in manufacturing flexible electronics. However, there are still trade-offs, especially in terms of resolution, materials compatibility, and the process itself. One of the direct printing approaches, inkjet printing, exhibited good quality printing within the flexible electronics application [5]. This method has better advantages than the traditional way due to the cost and the ability to deposit different kinds of ink materials. To add on, the line velocity of inkjet printing can get up to 50 mm/s, which is way more superior to the photolithography method, and this results in having taken less time to print over a large area [6]. Since this setup required pressure to pull the ink out from the nozzle [7], it can only print low-dense material with a range from (5 to 20 mPa s). Hence, there is no concrete additive manufacturing technique that will repeatedly produce high-quality resolution lines and low fabrication costs.

Fortunately, a new additive manufacturing technique, called electrohydrodynamic jet (e-jet) printing, has emerged as a differential method to inkjet printing, a low-cost system. E-jet printing used the applied electric field to drag the ink out of the nozzle and apply it to the substrate. This system can control the ink flow more accurately and eliminate the requirement of pressure to pull the ink out of the nozzle. E-jet is suitable for fast printing with a resolution of down to approximately 30nm features, and it’s also compatible with a good range of ink materials. Several studies have shown promising results for the usage of e-jet printing. For instance, Chang et al. combined triboelectric nanogenerators (TENG) with e-jet printing technique and achieved high-resolution printing, thus expanding the field of TENG [8]. Byeong et al. created 3D electronic components using different types of functional materials via the e-jet printing method, which is not able to achieve by using the traditional lithography method [9].
Also, the quality of graphene should not be neglected. It is because the good quality of graphene ink produced can be further developed into useful applications. One of the approaches that produced excellent and quality graphene is using the ball-milling exfoliation method [10]. For example, Li et al. developed a highly sensitive electrochemical sensing system where the ball-mill exfoliated graphene served as deposition substrate and prevented aggregation of Cu-BTC nanoparticles; the obtained material exhibited good conductivity and strong absorbability [10]. Fan et al. demonstrated an unique approach to fabricate Boron Nitride nanosheets (BNN) via hypochlorite-assisted ball milling, resulting in the potential application in catalysis [11]. Chen and her research members have successfully demonstrated high-quality edge selectively functionalized graphene nanoplatelets via ball milling method in large scale and low cost; thus opening opportunities in energy applications such as batteries, supercapacitors, and solar cells [12].

The ball-milling exfoliation method itself is not sufficient to have a stable graphene solution. Stabilizing agents such as proteins and polymers are required to ensure the exfoliation of graphene maximizes the process. To overcome this issue, Samad [13] has shown that adding Bovine Serum Albumin (BSA) can stabilize graphene through non-covalent bonding. It is believed that the hydrophobic of graphene bonds with the hydrophobic segments of BSA, whereas the hydrophilic segments of BSA bond with the water. Ma et al. have successfully constructed a drug system carrier in which the folic acid-grafted bovine serum albumin (FA-BSA) was used as a stabilizer, thus broadening the application of graphene oxide in drug delivery [14]. To add on, Chiu et al. have managed to open a pathway in developing highly sensitive clinical diagnostic applications via combining BSA protein with chemically modified graphene oxide sheet (GOS); the results obtained are much better in terms of sensitivity [15]. Proteins are cheap and can be easily found in the food industry. There are different kinds of protein that can be used to synthesize graphene, such as β-lactoglobulin (bovine milk),
lysozyme (egg white), ovalbumin (egg white), and hemoglobin (bovine blood) [16]. However, BSA is the best choice due to its highest efficiency exfoliation compared to other proteins [16].

In this work, we utilized the combination of BSA protein and ball-milling exfoliation coupled with shear force to achieve high-resolution printed lines via the e-jet printing method. We investigated the characteristics of graphene produced by using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Raman Spectroscopy, and Transmission Electron Microscopy (TEM). Lastly, we measured and described the conductivity of the printed lines.

### 2.2 Materials and Experimental Section

#### 2.2.1 Materials and Equipment

The materials used in this study were graphite (Synthetic powder, <20 μm, Sigma-Aldrich, St. Louis MO); Bovine Serum Albumin (BSA, > 98% of agarose gel electrophoresis, lyophilized powder, Sigma-Aldrich, St. Louis, MO); Polyethylenimine solution (PEI, 50% weight/volume, Sigma-Aldrich, St. Louis, MO); Poly(styrenesulfonate) solution (PSS, Molecular weight ~1,000,000 powder, Sigma-Aldrich, St. Louis, MO); Sodium Chloride (NaCl, purchased from Sigma-Aldrich, St. Louis, MO); Polyimide substrate (PI, thickness: 0.008mm, 100x100mm, Sigma-Aldrich, St. Louis, MO).

The equipment used in this study consisted of a four-axis CNC USB controller Mk3/4 controlled by PlanetCNC. A Sinometer Digital Multimeter (MS8261) was used to measure the conductivity of the printed lines. A JEOL 6000 Scanning Electron Microscope was used for SEM imaging to characterize the surface microstructure of the graphene printed surface. JEOL JSM2100 STEM was used for TEM imaging at 200kV accelerating voltage. AFM images were captured by Bruker Dimension Icon AFM and analyzed by NanoScope Analysis software. BWTEK Voyage confocal Raman system coupled with a CW laser as the energy source operating at the wavelength of 532nm was used to analyze the Raman spectra of the thin films.
2.2.2 Substrate Preparation

Kapton Polyimide (PI) was chosen as the substrate because of the tremendous thermal resistance that can withstand temperatures ranging from -250 to 400 °C [17]. Kapton treatment was needed to ensure that it is hydrophilic to the ink. First, the PI was washed with acetone on a petri dish. Next, the substrate was submerged in PSS (consists of 12mg/mL of distilled water and 0.5mol/L of NaCl) for 20 minutes. After that, the substrate was submerged in PEI (30mg/mL of distilled water and 0.5mol/L of NaCl) for another 20 minutes. The substrate was allowed to sit till dry for 1 hour.

Figure 2.2 (a) Schematic diagram of the shear exfoliation of graphite using ball-milling method [18] (b) Printed graphene lines on the substrate (c) Graphene ink used for experiment
2.2.3 Graphene Preparation

We used wet-ball milling via Vibro-Energy shaker mill [19] and blender mixing [20] methods as liquid exfoliation methods to produce graphene solution. The wet-ball milling method utilized the shear force created by the steel ball to exfoliate the graphene crystallites and produced high-quality few-layer graphene (FLG). 650 mg of graphite was mixed with 60 mg of BSA and distributed in 35 mL of distilled water. Next, a Vibro-Energy shaker mill was run for 90 hours at 300 rpm. 20 steel balls with a diameter of 8.7mm (11/32") and 10 steel balls with a diameter of 4.5mm (3/16") were added to all five containers. As for the blender mixing method, a standard kitchen blender was run for 1 hour at 17000 rpm. 20g of graphite was mixed with 605 mg of BSA and distributed in 100 mL of distilled water. Both graphene solutions were allowed to rest for 48 hours, enabling non-dispersed graphite particles to settle down at the bottom of containers. However, we believed that not all of the graphite could be exfoliated to the desired FLG. Therefore, the graphene solution was further centrifuge at 1500rpm for 45 minutes. Then, 90% of the volume from the top was taken out by pipette. This centrifugation aimed to completely remove the graphite from the solution and ensure the impurity of steel balls did not contaminate the solution.

2.2.4 E-jet Printing Procedure

Graphene ink was placed in a 5mL syringe, attached with a 10cm long polyurethane tube. The graphene ink was injected through a needle with an inner diameter of 0.51mm. The syringe was placed fix on the syringe pump with a continuous constant flow rate of 6 μL/s. A 3kV potential difference was applied between the needle and substrate to pull the ink out from the nozzle. During the printing process, a spherical meniscus formed when a liquid volume was being pushed out from the nozzle. This situation happened when the electrostatic force overcomes the surface tension of the liquid and was being deposited on top of the substrate [21]. We also observed that the ink droplets leave the tip of the needle after accumulation for
several seconds in the absence of electrostatic force. So, another advantage of utilizing the potential difference between electrodes is to control the flow rate of ink. A schematic diagram of the printer setup is shown in Fig 2.3.

Figure 2.3 Schematic diagram of the e-jet printing setup

2.3 Results and Discussion

2.3.1 Graphene Characterizations

2.3.1.1 Raman Spectroscopy

Raman spectroscopy was used to evaluate carbonaceous materials [22]. It has become a routine technique to gain graphene information, such as the structure, defects present in the material, or the number of layers obtained [23]. As shown in Fig 2.4, D (~1348 cm\(^{-1}\)), G (~1569 cm\(^{-1}\)), D’ (~1620 cm\(^{-1}\)), and 2D (~2695 cm\(^{-1}\)) contained information regarding the defect, lateral size, and the number of graphene layers exfoliated. The presence of graphene can be observed in the intensity of the D band, where \((I_D/I_G)_{\text{Graphene}} = 0.16\) compared to graphite sample where \((I_D/I_G)_{\text{Graphite}} = 0.02\) [13]. Besides that, we also observed the addition of D’ band shoulder peak, as shown in Fig 2.4. It is believed that the D and D’ bands were generated due to the shear force of the steel balls, which was essential in breaking the graphite into few-layer graphene (FLG). Eckmann et al. stated that the ratio of D band \((I_D)\) and D’ band \((I_D')\) could
numerically represent defects of sp³, vacancy, and boundary [24], which can deteriorate the electrical resistance of the FLG. Table 2 shows the value of $I_D/I_{D'}$ ratio as a function of the types of defects. Another thing we observed is that under the Raman characterization of graphene is that 2D band is not as peak compared to the graphite. This was likely due to the number of graphene aromatic domain. To determine defect source of the ball-milling exfoliation, we used Raman spectra to determine the mean lateral size of graphene platelets $<L>$. To calculate the lateral size, we used equation (1) where $k$ is the experimentally measure value of 0.17 and $(I_D/I_G)_{Graphite} = 0.02$ from the Raman spectra of graphite sample. The calculated $<L>$ is 0.12 $\mu$m.

$$<L> = \frac{k}{\left(\frac{I_D}{I_G}\right)_{Graphene} - \left(\frac{I_D}{I_G}\right)_{Graphite}}$$  \hspace{1cm} (1)

Figure 2.4 Raman spectra samples collected in 5 different spots [18]
2.3.1.2 SEM and AFM images of the printed surface

Scanning Electron Microscopy (SEM) is known to be capable of imaging a monolayer of graphene [26]. Fig 2.5 (a), (b), and (c) demonstrated the Scanning Electron Imaging of printed graphene lines after thermal annealing for 30 minutes. From Fig 2.5 (a), we took five different spots of the same line, and the average width of the lines was 695 \( \mu \)m. As for Fig 2.5(c), five different spots of the same line were taken, and the line’s average thickness was 5.062 \( \mu \)m. Atomic Force Microscopy (AFM) was used to analyze the graphene nanosheets thickness after the production. Figure 2.6 showed the height-profile images of graphene sheets disclosed a thickness of 7.6 \( \pm \) 2.3 nm, suggesting the presence of single-layer to few-layers graphene sheets.

<table>
<thead>
<tr>
<th>Type of Defects</th>
<th>( I_D/I_{D'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp3</td>
<td>13</td>
</tr>
<tr>
<td>Vacancy</td>
<td>7</td>
</tr>
<tr>
<td>Boundary</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure 2.5 Panel (a) is Scanning Electron Microscope (SEM) image at top view; scale bar = 500 μm while panel (b) is the SEM image of the surface morphologies cross section; scalebar = 20 μm and panel (c) is the SEM image of side view; scale bar = 5 μm

Figure 2.6 AFM image and height profile of graphene [19]
2.3.1.3 Transmission Electron Microscopy

We used TEM to examine the morphology of few-layer graphene and confirm the degree of exfoliation and defect-free graphene. The process started by depositing dried graphene on a Cu-grid. Based on figures 2.7 (a) and (b), we observed no cracks or defects on the graphene nanosheets, proving that the ball-milling method successfully produced graphene. In general, graphene sheets were analyzed by TEM and showed that the maximum lateral dimension of hundreds nm and proved that the exfoliation of graphite to graphene was successful.

Figure 2.7 TEM images of (a) single few-layer graphene; scale bar = 100nm and (b) Multiple graphene flakes folded together; scale bar = 100nm and (c) Distribution of graphene flake sizes
2.3.2 Post Processing and Electrical Conductivity

To improve the printed lines’ conductivity and stability, we performed post-processing of thermal annealing. Several articles have stated the benefits of thermal annealing. Kim et al. demonstrated various annealing temperatures to remove the polymer residue; and found out that annealing at a temperature from 300-400 °C leads to a significant reduction of residue [27]. To support this, Fig 2.8 has shown that there is less residue in panel (b) after undergoing thermal annealing for 30 minutes. Fang et al. investigated thermal annealing’s effects to eliminate contamination and restore clean surfaces of graphene [28]. Also, the thermal annealing process can reduce FLG flake-to-substrate defects [23, 28]. In Fig 2.9, we looked into how annealing temperature at 280 °C at different durations affect the sheet resistance and found out that 30 mins are sufficient enough to reduce the sheet resistance to the lowest, which is 41.75 Ω/sqr. In Fig 2.10, we looked into how annealing temperature ranging from 50 to 280 °C will affect the sheet resistance. The results showed that the sheet resistance dropped significantly when the temperature goes beyond 200 °C.

Figure 2.8 SEM image of cross section (a) before annealing and (b) after annealing
Figure 2.9 The change of sheet resistance with respect to annealing time at 280 °C

Figure 2.10 The change of sheet resistance with respect to changes in annealing temperature
Equation (2) can be used to calculate the conductivity of the graphene, where \( l \) is the length of the lines, \( w \) is the width and \( t \) is the thickness of the lines, and \( R \) is the resistance of the lines. The thickness, \( t \), and width, \( w \), can be measured through SEM (Figure 2.5 (b) and (d)) at five different points along the printed lines and averaged the values for conductivity measurement. Resistance can be measured by using a VersaSTAT four Potentiostat Galvanostat. The conductivity that we measured was approximately 63.96 S/m.

\[
\sigma = \frac{l}{wtR}
\]  

(2)

2.4 Conclusion

In this chapter, we found a feasible method using a combination of wet ball milling and BSA to produce high-quality FLG nanosheets. The customized graphene deposited ink on the flexible substrates during the e-jet printing process. It has shown promising results in terms of material stability and electrical conductivity. The shear force generated by the steel balls managed to reduce graphite to graphene platelets (~3-4 layers). We also characterized the graphene by using Scanning Electron Microscopic (SEM), Atomic Force Analysis (AFM), Transmission Scanning Electron (TEM), and Raman spectroscopy. Next, we had justified that when the printed lines were annealed at 280 °C, the sheet resistance was reduced to 41.75 \( \Omega \)/sqr. The values obtained from SEM were used in equation (1) to measure the conductivity of lines. The conductivity was calculated to be 63.96 S/m.
2.5 References


CHAPTER 3.  E-JET PRINTED STRETCHABLE SENSOR BASED ON PDMS FILMS

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A paper under review for submission to Journals of Biosensors

3.1 Introduction

Wearable electronics is a field of technology that has attracted huge interest due to consumer demand. Besides utilizing it in consumer electronics, it can be used in physical activity tracking [1], health monitoring [2], and human motion detection [3]. In order for the device to function properly, the strain sensor is a vital part that allowed mechanical deformation to be converted into electrical signals. Wearable sensors need to satisfy the requirements of stretchability, flexibility, and robustness. Due to these reasons, different flexible strain sensors have been developed using nanowires [4], fibers [5], and metal nanoparticles [6]. However, the fabrication of stretchable strain sensors still needs to be improved so that they can be used in different applications.

To overcome these limitations, researchers have proposed composite materials such as graphene composite [7], conductive composite film [8], thermoplastic composite [9], and thermoset composite [10] to be investigated in different applications. Until recently, researchers have illustrated that carbon nanomaterial-based sensors [11] could achieve excellent success because of their electrical and mechanical properties [12]. Several articles [13-15] of using graphene sheets on flexible substrates to produce sensor strains have been described. Unfortunately, it has been shown that strain sensors made of graphene sheets have low stretchability (strain=5%) due to the brittleness of the sheets. Alternatively, graphene flakes have attracted great attention, especially in the engineering field, because of their high
mechanical, electrical, and thermal properties. These unique properties of graphene flake possessed have created an opportunity to manufacture high-quality strain sensors that can be utilized in a new field.

In this paper, we utilized graphene flakes to fabricate a new strain sensor for a high stretchability on PDMS substrate through our e-jet printer. We also investigated the strain sensing performance under stretching and bending. Resistance and conductance of graphene were collected and measured. Also, we looked into the relationship between the I-V curve of the sensor, which showed that the suggested sensor could be used as a strain sensor.

3.1.1 Introduction to PDMS

The material for the experiment in this chapter is Polydimethylsiloxane (PDMS), which is a silicone-based polymer. It is a widely used silicon-based organic polymer and is known for its unusual rheological properties. Its applications can be varied from contact lenses to medical devices and elastomers. PDMS is transparent and considered to be inert, non-flammable, and non-toxic.

3.1.2 Microstructure of PDMS

The chemical formula for PDMS is \((\text{H}_3\text{C})_3\text{SiO}[\text{Si(CH}_3)_2\text{O}]_n\text{Si(CH}_3)_3\), where \(n\) is the number of repeating monomers [\text{SiO(CH}_3\text{)}_2\text{]} units. Its short formula is shown in Fig 3.1. The industrial synthesis starts from dimethyl chlorosilane and water following the reaction:

\[
\text{Si} + \text{H}_2\text{O} + \text{HCl} \rightarrow (\text{H}_3\text{C})_3\text{SiO}[\text{Si(CH}_3)_2\text{O}]_n\text{Si(CH}_3)_3
\]

Fig 3.1 PDMS chemical formula [16]
The network of PDMS is fabricated by crosslinking these polymer chains. The long PDMS polymer chains have vinyl groups at each end. The short crosslinker is polymethyl-hydro siloxane, which links the PDMS chain.

### 3.1.3 PDMS Characteristics

Table 3.1 shows the physical properties of PDMS. It has unique flexibility of Young’s elastic modulus of (~1-3 MPa) because of the lowest glass transition temperature of any polymer ($T_g = -125 ^\circ C$). It has heat resistant of more than 400 °C [17]. PDMS is also optical transparency (240-1100 nm) and displays low surface tension around 21 mN/m.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductivity</td>
<td>$2.9 \times 10^14 \Omega$*cm</td>
<td>[18]</td>
</tr>
<tr>
<td>Heat Conductivity</td>
<td>0.27 W/m*K</td>
<td>[19]</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>21 mN/m</td>
<td>[20]</td>
</tr>
<tr>
<td>Glass Transition Temperature</td>
<td>$-125 ^\circ C$</td>
<td>[21]</td>
</tr>
<tr>
<td>Optical Transparency</td>
<td>240 – 1100 nm</td>
<td>[22-23]</td>
</tr>
<tr>
<td>Young’s Elastic Modulus</td>
<td>~1-3 MPa</td>
<td>[24]</td>
</tr>
</tbody>
</table>

PDMS is a low-cost material, and it has a good ability to seal with other surfaces without using other adhesives. It is not brittle when compared to silicone devices. However, when a strong bending and stretching force is performed upon the substrate, it will eventually break.

### 3.2 Materials and Experimental Section

#### 3.2.1 Materials and Equipment

The materials used in this study were graphite (Synthetic powder, <20 μm, Sigma-Aldrich, St. Louis MO); Bovine Serum Albumin (BSA, > 98% of agarose gel electrophoresis,
lyophilized powder, Sigma-Aldrich, St. Louis, MO); Polyethyleneimine solution (PEI, 50% weight/volume, Sigma-Aldrich, St. Louis, MO); Poly(styrenesulfonate) solution (PSS, Molecular weight ~1,000,000 powder, Sigma-Aldrich, St. Louis, MO); Sodium Chloride (NaCl, purchased from Sigma-Aldrich, St. Louis, MO); Polyimide substrate (PI, thickness: 0.008mm, 100x100mm, Sigma-Aldrich, St. Louis, MO).

PDMS samples were synthesized with the same composition: Sylgard 184 silicone elastomer base and Sylgard 184 silicone elastomer curing agent. These samples have different base/curing ratios, which means a different degree of crosslinking. The higher the degree of crosslinking, the stiffer the sample. Similarly, the lower the degree of crosslinking, the softer the PDMS is.

VersaSTAT 4 Potentiostat Galvanostat was used to measure the electrical characterization of voltage and current of the printed lines. THORLABS stretching machine was used to experiment with different stretching % on the thin film. A Sinometer Digital Multimeter (MS8261) was used to measure the resistance of the printed lines.

3.2.2 Transfer Printing Process

To print high-resolution aqueous solution graphene ink and avoid the coffee stain effect [25], we have to find a suitable substrate that can absorb immediately. We performed the e-jet printing onto a PI film and followed by transferring the graphene patterns to PDMS to reduce the issue. The graphene ink was printed a few times to obtain a high uniformity, as shown in Fig 3.2a. When more prints are executed, the area increases and the network starts to be conductive at 3 to 5 prints.

PDMS was prepared by mixing the base with the curing agent in a 10:1 ratio weight and mixing it for 10 minutes. After that, put it into the vacuum chamber to desiccate for at least 20 minutes before casting them on the pattern’s surface as shown in Fig 3.2b and let it sit for 1
hour before placing it into the oven cure for 1 hour at 100 °C. Then, the cured PDMS substrate can be peeled off in Fig 3.2c and cut into different sizes and shapes for experimenting.

![Fig 3.2 The transfer printing process: (a) E-jet printing of graphene ink on a PI film; (b) Casting PDMS over the printed lines; (c) PDMS peeled off after curing](image)

3.2.3 Characterizations

VersaSTAT 4 Potentiostat Galvanostat was used to measure the electrical characterization of the printed layers. To obtain the I-V curve, the probes were connected to the electrodes, and a voltage was applied from -10 to +10 V, and the graph showed that the voltage is directly proportional to the current. Fig 3.3 showed the experimental setup used for stretching the proposed strain sensor, where the sensor is placed on the stretching machine. A bending test was performed on the proposed strain sensor to test out its flexibility. Fig 3.4 shows that the substrate was bent with consistent contact with different diameters on the index finger.
Fig 3.3 Schematic diagram of the experimental setup used for stretching the proposed strain sensor, where the sensor is placed on the bending machine.

Fig 3.4 The sensor is attached to the finger for motion detection experiment under different bending diameters.
3.3 Results and Discussion

Figure 3.5(a) and (b) showed the schematic illustration to describe the stretching behaviors. When applying strain force, graphene flakes move apart, and the initial micro-cracks expanded, causing the overlapping area between flake and flake to decrease. As a result, the resistance of the strain sensor increased under the stretching phenomenon. To understand the I-V characteristics over different stretchability, a sweeping voltage of -10 to +10 V was applied across the terminals of the fabricated strain sensor in Fig 3.6. The graph exhibited a linear relationship between voltage and current. The electrical resistance of the sensors was also linearly varied with their stretching. Likewise, we measured the I-V characteristics over different bending diameters of strain sensors in Fig 3.7, and the graph illustrated a linear relationship between voltage and current. Also, the slope of the I-V curve can be used as a strain sensor to measure bending, indicating that the electrical resistance can linearly estimate against their bending.

![Schematic Illustration](image)

Figure 3.5 (a) Schematic explanation of the deformations under 0%, 10%, 20% and 30% stretching. (b) Schematic explanations of the active layer on the substrate. During stretching, the gap between graphene flakes is increased, leading to the increase of electrical resistance.
Figure 3.6 I-V curves under different stretching %

Figure 3.7 I-V curves under different diameter
Now, we looked into how the strain sensor can be applied to real-life applications. Firstly, we attached the strain sensor to the index finger. Then, we measured and collected the sensor’s electrical resistance by bending different diameters of the finger. In Fig 3.8, the electrical resistance decreased linearly under bending until 2cm. The change of electrical resistance was mainly due to the overlapping graphene flakes phenomenon on the film. The data was measured and averaged for five samples at different bending diameters to minimize the resistance error. Next, we will look into how the proposed strain sensor performed under stretchability analysis. The electrical resistance in Fig 3.9 shows the sensor’s electrical resistance increased linearly up to 25% stretching. But, when we increased the elongation beyond 25%, we observed a nonlinear behavior in the graph. It is most likely due to the cracks in the film. Similarly, we also measured five samples at different stretching % to minimize the error in resistance. Based on the experiment results above, the proposed sensor has good performance on stretching and bending.

![Figure 3.8 Resistance variation under different bending diameters](image-url)
Figure 3.9 Resistance variation under different stretching %

Figure 3.10 Cycles of elongation and relaxation at 1cm bending diameter
We also looked into the effects of temperature on the proposed strain sensor by using VersaSTAT 4 Potentiostat Galvanostat to measure the I-V curves at different temperatures. Fig 3.11 showed that when the temperature increases from 20 °C to 70 °C, there is no change in the strain sensor response. Next, when increasing the temperature beyond 70 °C, there is an increase in current till 110 °C. When the temperature rises to 140 °C, the current varied from 400nA to approximately 500nA. Based on the results, we can say that the proposed strain sensor will remain stable in response until temperature 110 °C. In other words, the strain sensor can operate functionally under 110 °C.

Figure 3.11 I-V curves measured at different temperatures
Next, we are trying to observe the stability of the sensor under static loading. We applied a 25% strain on the proposed sensor for 10 minutes, the drift of electrical resistance was approximately 1%, as shown in Fig 3.12. Similarly, the sensor was bent down for 10 minutes at 1 cm, and the drift of electrical resistance was 0.05%, as shown in Fig 3.13. The results showed that the proposed sensor is more stable in terms of electrical resistance under bending than stretching. Nonetheless, the strain sensor showed consistent stability in stretching and bending, which indicated that the strain sensor could be used for real-life applications. I would like to emphasize that the finger-bending data is just proof-of-concept and the repeatable and properly collected data are from the DMA test, which will be discussed later on.

Figure 3.12 Sensing performance of 10 mins under 25% stretching
To test for displacement performance, the sensor was placed on the dynamic mechanical analyzer to achieve different deformations of the substrate. Figure 3.14 showed the normalized sensor resistance change, $\Delta R/R$ (where $R$ is the initial resistance, and $\Delta R$ is the difference between the resistances at bending and relaxation states). We observed that the $\Delta R/R$ increased with the bending (displacement) of the sensor. This is due to the cracks formed in the graphene ink layer. 5% of $\Delta R/R$ was achieved with a bending limit of 28 mm. The experiments were repeated five times for each displacement value, and the blue dots in Fig 3.14 represented the average $\Delta R/R$ under different displacements. The proposed strain sensor that was fabricated using the e-jet printing method can provide higher sensing sensitivity than the ones fabricated using lithography or inkjet printing method under the same bending conditions.
Likewise, the proposed strain sensor was fixed on the dynamic mechanical analyzer and bend in the middle to characterize sensing performance under different tension levels. We used a multimeter was used to record the resistance values under different strains. The experiments were conducted five times for each strain value to minimize the average $\Delta R/R$ under varying tension levels. The graph in Fig 3.15 exhibited a linear increase relationship between different bending strain and $\Delta R/R$, where the increasing strain range up to 0.053% which the $\Delta R/R$ of $0.9 \pm 0.4\%$ was achieved. The results demonstrated that the proposed strain sensor could achieve a good and consistent sensing performance.

Figure 3.14 Change of resistance to different displacement when the sensor is bent
3.4 Conclusion

A highly stretchable graphene-PDMS was fabricated using the e-jet printing method. We have demonstrated stretchability up to 30% and bending up to 27mm displacement. Also, the I-V curve illustrated a linear relationship between current and voltage, which suggested that the proposed sensor demonstrated ohmic resistor behaviors. The proposed sensor suggested that it can function normally in an environment temperature below 110 °C. On the whole, the proposed sensor can be used in wearable electronic applications because of its high stretchability and flexibility.
3.5 References


CHAPTER 4. GENERAL CONCLUSION

4.1 General Conclusion

In this thesis, two projects are conducted which are the e-jet printing of organic inks on organic substrate and e-jet printed stretchable sensor based on PDMS films.

In Chapter 2, we introduced an easy and inexpensive ball-milling exfoliation method to produce few-layers graphene. This method utilized the shear force of steel balls to further exfoliate the graphene sheets with the addition of stabilizing agent called Bovine Serum Albumin (BSA). The customized printer deposited graphene ink on the flexible substrates during the e-jet printing process with controlled parameters. Raman Spectroscopy was used to gain graphene information, such as the structure, defects present in the material, or the number of layers obtained. The Scanning Electron Microscope (SEM) analysis disclosed the effects of printed lines before and after annealing, showing that there is less residual spotted on the printed surface. The sheet resistance was measured to be 41.75 $\Omega$/sqr, and the conductivity was calculated to be 63.96 S/m.

In Chapter 3, we used graphene flakes to produce a new strain sensor for a high stretchability on PDMS substrate through our e-jet printer. We will also investigate the strain sensing performance under stretching and bending. Experimental results show that the substrate has demonstrated stretchability up to 30% and bending up to 1cm diameter. Also, the I-V curve illustrated a linear relationship between voltage and current, which suggested that the proposed sensor demonstrated ohmic resistor behaviors. The proposed sensor suggested that it can function normally in an environment temperature below under 110 °C. Besides, we also indicated the stability of the proposed sensor under stretching and bending for 10 minutes, respectively. On the whole, the proposed sensor can be used in wearable electronic applications because of its high stretchability and flexibility.
4.2 Future Work

In Chapter 2, the custom 3D printer that we used for conducting the experiment has difficulty making use of the G-code effectively during the printing process. Due to the current issue, we sometimes have to manually print the lines on top of the substrate, which is time-consuming. To improve the resolution of the printed lines, we could modify the current printer with a higher accuracy motor or update the CNC software consistently to make sure it is up to the latest version.

In Chapter 3, we managed to get the preliminary results on how stretching and bending acted upon the PDMS substrate. In our case, the PDMS substrate is fabricated based on the 10:1 ratio of base to curing agent. The next step that we could explore is by finding the best PDMS blending ratio for the proposed strain sensor and test for its sensitivity.