Development of a Novel Printed and Flexible Surface Enhanced Raman Specopy (Sers) Substrate for Detection of Cocaine

Farah Mazin Aljanabi

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DEVELOPMENT OF A NOVEL PRINTED AND FLEXIBLE SURFACE ENHANCED RAMAN SPECOPY (SERS) SUBSTRATE FOR DETECTION OF COCAINE

by

Farah Mazin Aljanabi

A thesis submitted to the Graduate College in partial fulfillment of the requirements for the Degree of Master of Science in Engineering Western Michigan University June 2017

Thesis Committee:

Massood Z. Atashbar, Ph.D., Chair
Bradley J. Bazuin, Ph.D.
Paul D. Fleming, Ph.D.
In this thesis, the author focuses on the design and fabrication of a novel surface enhanced Raman spectroscopy (SERS) substrate that could potentially be employed for the detection of illicit drugs. Raman spectroscopy based optical detection has been extensively employed as a qualitative and quantitative analytical method.

The author has worked on two research projects, which are both focused on the development of printed SERS substrate for the detection of cocaine. The first project is based on gravure printing of silver nanoparticle (AgNP) based ink on flexible and stretchable thermoplastic polyurethane (TPU) substrate. The fabricated substrate dimensions are 1.5 × 1.5 inches, and the average thickness and roughness for the printed AgNP film was measured to be 7.78 µm and 0.18 µm, respectively. An enhancement factor (EF) of three, in the intensity of Raman signal of cocaine on the printed SERS substrate, was observed when compared to target molecules absorbed on a bare TPU substrate. This EF is based on the large electromagnetic fields, created by interaction of the AgNPs with light.

The second project is focused on the fabrication of a rougher surface of the SERS substrate to amplify the generated electromagnetic fields that could result in a larger enhancement of the Raman signal intensity. The SERS substrate was designed with dimensions of 3 × 0.5 inches, and was fabricated by gravure printing the AgNP ink on a stretched (25%, 50%, 75% and 100%) TPU substrate to form a wrinkled nanostructure SERS surface. An EF of 2, in the intensity of Raman peak of cocaine for the 25% stretched SERS substrate with an average roughness of 1.57 µm was observed, when compared to the Raman signal of cocaine on the non-stretched SERS substrate. And an EF of 6, in the intensity of Raman spectra of cocaine for the 25% stretched SERS substrate when compared to the Raman spectra of cocaine on the bare TPU substrate.
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Also, I want to thank everyone in the Electrical and Computer Engineering (ECE) Department, Chemical and Paper Engineering (ChP) Department for the support and all resources provided to me during the course of this thesis work.

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Farah Mazin Aljanabi
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CHAPTER I
INTRODUCTION

1.1 Motivation

Humans use their sensory organs to interact with the surrounding environment and translate the sensory input into stimuli that permit actions and reactions [1]. Due to the limitations of our senses, there is a continuous need for devices and sensors that could help in different fields of our life [2]. In recent years, several achievements in the field of printed electronics (PE) have been achieved including the development of flexible and stretchable electronic devices for multiple applications such as robotics [3], monitoring temperature [4] and wearable devices [5].

Additive manufacturing techniques are used in the fabrication of PE. These techniques include gravure [6], inkjet [7], screen printing [8] and flexography [9]. These manufacturing techniques have multiple advantages when compared to silicon based technology that often results in the waste of material involves complex photolithographic patterning techniques, and requires high temperature and high vacuum deposition processes. Furthermore, silicon based electronics are rigid, and therefore cannot be used for many applications that need a direct conformal contact with the human body. PE devices and technology continues to grow and is expected to have a significant impact on the electronics market. The market for PE components and devices is forecasted to increase to $300 billion within the next 10 years [10]. Among the multiple types of printing techniques, gravure printing has proven its capability as a high quality and high speed method employed for the deposition of different materials on flexible substrates [11,12].

Illicit drugs are widely used in the modern world, and unfortunately are closely associated with a rise in violence and crime, in addition to their harmful effect to human health [13]. Even though the detection and identification of illicit drugs has been done by using several techniques, Raman spectroscopy based optical detection has been widely preferred as a rapid, reliable and non-destructive technique for detection [14,15]. Surface enhanced Raman spectroscopy (SERS) provides a sensitive and selective analytical
detection technique for bio-chemical sensing by utilizing nanoscale metallic surfaces that enhance the electromagnetic fields resulting in an enhanced Raman spectrum of target molecules [16-18].

1.2 Author’s Contributions

The author’s research work has resulted in two conference publication and three journal publications (in progress for submission). The publications directly related to the research performed for this thesis have been marked with “*”. The author was also awarded the Western Michigan University Travel Grant to attend the IEEE Sensors Conference in Orlando, Florida in November 2016.

Journal Papers:

Conference Papers:

1.3 Thesis Organization

In this thesis, the author presents in detail two research projects that were performed during the course of her Master’s studies. This thesis will provide background information, describe aspects of PE technology required and used, discuss the projects performed, and demonstrate sensor performance in seven chapters, outlined as follows.

Chapter 2 presents a background of sensors and brief explanation of numerous kinds of sensors. Chapter 3 discusses different printing techniques that are typically used in the fabrication of PE. Chapter 4 focusses on Raman scattering theory and SERS as method of detection and analysis of bio-chemicals. Chapter 5 discusses the first research project that involves the detection of cocaine using gravure printed AgNP based SERS substrate. Details provided include the fabrication process, experimental setup, and measurement results. Chapter 6 discusses the second project involving the fabrication of a wrinkled SERS substrate for the detection of cocaine, including the theory, design, fabrication, and measurement results. Finally, in Chapter 7 the author concludes with a summary of the thesis along with suggestions for future work.
1.4 References


CHAPTER II
INTRODUCTION TO SENSORS

2.1 Introduction

A sensor converts physical properties such as pressure, temperature, speed and humidity into a signal that can be measured electrically [1]. In this chapter, the basic definition of numerous types of sensors will be introduced with their characteristics. A sensor is a device that can be considered as the interface between real world physical phenomenon, such as light, sound and heat, and the electronic circuits. Sensors converts the energy that is derived from the physical phenomenon into a suitable electrical signal output [2].

Humans have advanced their capabilities in different dependent stages throughout history (Fig. 2.1). In the past century, they started to develop their mechanical powers by the fabrication of unprecedented machines and devices such as the steam engine and electrical motor, which led to the industrial revolution of mechanization. Then, they increased their competence by inventing the computer and then the Internet giving rise to the information age. With continued advancement of information processing and the advancement and miniaturization of computers, another significant period has emerged involving sensors. During the past decade, sensorization has emerged, which has led to significant industrial and practical automation and robotization by combining mechanization, information technology and sensors [3]. The past several years have seen a great rise in the development of sensors as well as the number of applications [1].

Sensors can be divided into two categories depending on the operation technique; active and passive sensors. An active sensor is a device that requires an external source of excitation such as a resistive strain gauge or a pressure sensor, while a passive sensor is a device that does not require an external power source, which means that the sensor can generate its own energy from the phenomenon being measured such as photodiodes [4]. Table 2.1 provides some typical sensors along with their inputs and outputs.

Another classification for the sensors is based on its simplicity or complexity. A simple sensor or a direct sensor uses the physical effect to transform the excitation
stimulus into an electrical signal. A complex sensor usually needs a supplementary transducer to perform the same transformation as the direct sensor [5].

![Figure 2.1: History of industrial automation [3].](image)

Table 2.1 Examples of sensors and their outputs [6].

<table>
<thead>
<tr>
<th>Property</th>
<th>Sensor</th>
<th>Input type</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>LVDT</td>
<td>Active</td>
<td>AC Voltage</td>
</tr>
<tr>
<td>Pressure / Force</td>
<td>Piezoelectric</td>
<td>Passive</td>
<td>Voltage</td>
</tr>
<tr>
<td></td>
<td>Strain Gauge</td>
<td>Active</td>
<td>Resistance</td>
</tr>
<tr>
<td>Acceleration</td>
<td>Accelerometer</td>
<td>Active</td>
<td>Capacitance</td>
</tr>
<tr>
<td>Light Intensity</td>
<td>Photodiode</td>
<td>Passive</td>
<td>Current</td>
</tr>
<tr>
<td>Temperature</td>
<td>Thermister</td>
<td>Active</td>
<td>Resistance</td>
</tr>
<tr>
<td></td>
<td>Thermocouple</td>
<td>Passive</td>
<td>Voltage</td>
</tr>
<tr>
<td></td>
<td>Silicon</td>
<td>Active</td>
<td>Voltage / Current</td>
</tr>
<tr>
<td></td>
<td>RTD</td>
<td>Active</td>
<td>Resistance</td>
</tr>
</tbody>
</table>

2.2 Sensing Systems

Sensors are devices that convert the physical stimulus such as sound, motion, pressure, heat and light into an electrical signal. Transducers are devices that have the
ability to transform the energy from one form to another. The difference between sensors and transducers is that the sensors perform transducing actions, while transducers sense some physical quantities [6]. On the other hand, actuators may be implemented as sensors but in a reversed direction which means that actuators can convert the electrical signals to an action such as a mechanical movement. As a result, sensors and actuators may be considered as different kinds of transducers [7].

Figure 2.2 presents a system that consists of a sensor, modifier and transducer along with a power supply that is connected to all of them. If the sensor is passive, there is no need to use a power supply because the sensor will self-generate its energy, similar to a photodiode that generates voltage by the impact of the light. The modifier is used for modification purposes such as amplifying or conditioning the electrical signal [6].

![Figure 2.2: General measurement system [7].](image)

### 2.3 Types of Sensors

The classification of sensors depends on the type of energy that is being transformed from one form to another. In this section, the major kinds of sensors will be discussed.
2.3.1 Mechanical Sensors

The principle behind the operation of mechanical sensors is the detection of the deformation and deflection of the materials in order to convert them to electrical signals [8]. Mechanical sensors can be used to measure many properties such as stress, acceleration and pressure.

An example of a mechanical sensor is an accelerometer that is used to measure acceleration, which is a substantial flow for absolute motion measurement and vibration sensing. There are two typical configurations of the accelerometer, active and passive. The selection of the type of an accelerometer depends on the application. For example, the active accelerometer cannot be used for a static or DC measurement [8]. Fig. 2.3 shows a typical deflection type seismic accelerometer [8]. In this case, a seismic mass is suspended by a spring inside a rigid frame. The frame is connected to the vibrating structure; hence, when vibration occurs, the mass stays fixed to pick up the relative displacement. The accelerometer can be classified as electrical or mechanical depending on the practical transducers operation depending on the mechanical properties such as distortion of the spring or fluid dynamics, or on electrical and magnetic forces.

![Figure 2.3: Typical deflection seismic accelerometer [8].](image)
2.3.2 Thermal Sensors

Temperature is defined as the specific amount of heat energy in any system or object [7]. Heat energy is often related to molecular energy (friction, oscillation and vibration of particles within the molecule). Temperature sensors are used to measure changes in heat energy (temperature change) by detecting changes in a physical quantity, such as output voltage or resistance that corresponds to the temperature change [7].

The input signal of the thermal sensor is transduced into an output signal in two sequential steps: (a) transducing the input signal as a physical quantity to a thermal quantity and (b) the thermal quantity is transduced into an electrical signal [8]. Temperature sensing has been classified into two main types: contact and non-contact.

Contact temperature sensing requires a direct physical contact with the object under measurement, while the non-contact depends on interrupting the radiant energy of a heat source in the form of energy emitted in the infrared portion of the electromagnetic spectrum [6]. Medical infrared thermometry is an example of a temperature sensor, which is used to measure the temperature of the human body. It is based on measuring the skin surface temperature that gives an estimation of the internal body temperature. Moreover, it depends on the environment condition and skin blood perfusion; therefore, it may exhibit a perceivable error. On the other hand, the IR thermometer is widely used due to its accuracy and ease of use. It is based on placing the IR thermometer probe into the ear canal that gives a highly accurate reading because of the tympanic membrane inside the canal, which has a very close temperature to that of the blood [9].

Figure 2.4 shows a block diagram of a thermal sensor [8,10]. The thermopile IR sensor is designed inside a metal casing that is connected to a heater. Before using the thermopile for detecting the human body temperature, the heater warms the IR sensor up to 37 °C. For a healthy patient, the thermal gradient between the sensor and the patient is usually close to zero, but for a patient with a fever the thermal gradient is in the range of 2-4 °C.
2.3.3 Acoustic Sensors

Acoustic sensors are devices that are used to measure the chemical, physical and biological quantities by utilizing the elastic waves at various frequencies, often in the range of megahertz to gigahertz [1]. Acoustic sensors are very sensitive, specifically for chemical vapor and gas sensing. Since 1918, when sonar became viable, acoustic waves have been successfully utilized to determine the underwater objects features such as the position, velocity and tendency in different applications for both the commercial and military services [1,11].

The acoustic waves are considered as mechanical pressure waves and, therefore, microphones may be considered as a kind of acoustic sensors as they have the same basis as a pressure sensor. Basically, all microphones consist of two major components; a moving diaphragm and a displacement transducer that transform the diaphragm deflection into an electrical signal (Fig. 2.5). A condenser microphone is designed with a
silicon diaphragm that is useful in two ways: transforming the acoustic pressure into displacement and to act as a mobile plate of a capacitor [5].

![Circuit Diagram](image1)

**Figure 2.5**: The condenser microphone with a mechanical feedback: (a) A circuit diagram; (b) Integrated electrodes on the diaphragm [5].

Figure 2.5 shows the circuit diagram of the condenser microphone with a mechanical feedback from the output of the amplifier to the diaphragm for improving the characteristics of the condenser microphone [5]. The interdigitated electrodes of the microphone have two phases: first is converting the diaphragm displacement into voltage at the input of the amplifier, while the second is to convert the feedback voltage into a mechanical deflection which improves the frequency range, linearity, lowers the sensitivity and reduces the deflection.
2.3.4 Chemical and Biological Sensors

Chemical and biological sensors are devices used to detect and quantify a specific matter or analyte depending on the chemical or biological reactions [12]. The chemical or biological sensors are often used to detect and recognize a specific molecular species and then convert the recognition outcome into an electrical signal. The typical chemical sensor or biosensor associates the detection and quantification in the same system.

![Diagram of a chemical/biological sensor]

Figure 2.6: Basic components of a chemical/biological sensor [12].

The working of a chemical and biological sensor is based on two stages: (a) an interaction between the analyte to be measured and the active surface of the sensor, (b) the interaction between the analyte and the sensor surface needs to be detected by a transducer. In addition, the support software that is used to report and amplify the output signal of the transducer. Figure 2.6 illustrates the components of a chemical or biological sensor [12].
2.3.5 Optical Sensors

Optical sensors are based on the phenomenon of converting light rays into electronic signals including measuring the physical quantity of light and then translating it into a form that is readable by an instrument [3]. An optical sensor is generally a part of a larger system that integrates a reference source of light, a measuring device as well as the optical sensor.

Optical sensors are used for measuring radiation properties, such as intensity, polarization and spectral distribution, and they are of two types: thermal detectors and photon detectors [3]. As an example of optical sensors, an electro-optical cardiac sound sensor is shown in Fig. 2.7. It used in medical applications such as a clinical diagnosis tool [13].

The advantage of the electro-optical cardiac sound sensor is its small size, light weight, electrical sensitivity and the wide bandwidth. This device consists of several transmitters and receivers that are used to increase the signal-to-noise ratio and decrease the sensitivity to the skin reflection properties. When the wall chest vibrates, the device will detect the time varying amount of light and conform the inverse square law with distance.
2.4 Sensors Characteristics and Terminology

This section explains the relationship between the input stimuli and the output electrical signal of the sensors. The static characteristics of sensors will be discussed, which can be measured after the transient effects, or in other words, after stabilizing to their final result or steady state.

2.4.1 Sensitivity

Sensitivity is the relation between the input and output signal. Usually, the input is a physical stimulus and the output is an electrical signal. Sensitivity can be defined as the ratio of the smallest change between the output electrical signal and the input physical signal. Figure 2.8 shows the sensitivity in terms of the slope ($\Delta y/\Delta x$) of an output curve as well as the sensitivity error which represents the departure from the ideal slope of the characteristic curve [2].
2.4.2 Selectivity

The selectivity of any sensor is its capability to detect a single component in the existence of other components. For example, gas sensors are capable of detecting only one kind of gas, while it is in a mixture that contains multiple gases. An example is an oxygen sensor that produces a response only towards oxygen; however, it does not show any reaction to other gases such as CO\textsubscript{2} or NO\textsubscript{2}, and this response is known to be selective [14]. Equations (2) and (3) illustrate the relationship of a sensor when it is sensitive to measurands \(x_1, x_2, ..., x_n\) [15].

\[
y = y_0 + \frac{\sigma_y}{\sigma_{x_1}} \Delta x_1 + \cdots + \frac{\sigma_y}{\sigma_{x_n}} \Delta x_n \tag{1}
\]

\[
y = y_0 + S_1 \cdot \Delta x_1 + \cdots + S_n \cdot \Delta x_n \tag{2}
\]

Where,

\(y\) = the output of the sensor in the presence of measurands,

\(y_0\) = the output of the sensor in the absence of measurands,

\(S\) = sensitivities to different measurands.
Equation (3) illustrates the selectivity to a specified measurand such as $x_1$, when $j \neq 1$.

$$Sel_{x_1} = \frac{\sigma_y/\sigma_{x_1}}{\sigma_y/\sigma_{x_j}}$$ (3)

The sensitivity of an array of $m$ sensors is shown in Eq. (4), each sensor is sensitive to $n$ different measurands that leads to the beneficial outcome for each sensor.

$$S = \begin{bmatrix} \frac{\sigma_{f_1}}{\sigma_{x_1}} & \cdots & \frac{\sigma_{f_1}}{\sigma_{x_n}} \\ \vdots & \ddots & \vdots \\ \frac{\sigma_{f_m}}{\sigma_{x_1}} & \cdots & \frac{\sigma_{f_m}}{\sigma_{x_n}} \end{bmatrix}$$ (4)

According to the same concept, the selectivity of the complete array or for a single sensor can be characterized, in terms of the array’s ability to recover the $n$ value.

### 2.4.3 Accuracy

The accuracy of a sensor can be expressed as the variation between the expected and the actual values at the output of the sensor. Obviously, it is the specialty that demonstrates the capability of any measuring instrument to obtain a result that is close to the ideal value of the measured quantity [2]. The accuracy of a sensor can be calculated by keeping track of a static calibration process, therefore the calculation process depends on keeping all the sensor input parameters constant except the one that need to be studied. The calibration curve, which is the resultant plot against the input values, is used to measure the accuracy which is the difference between the instrument reading and the true value [16].

$$\text{Accuracy} = \text{Result} - \text{True value}$$ (5)

### 2.4.4 Resolution

Resolution can be defined as the smallest change in the input parameters that is substantial enough to be discovered as a detectable change at the output [16]. The output signal of some sensors will not be consistent, when the input changes continuously. The output may vary in minimal steps in some applications such as the potentiometric transducer, that its output signal change is only allowed upon a specific variation in the
input signal. Thus, the resolution is the amplitude of the input signal variation that results in the output lowest step, under specific conditions [5].

2.4.5 Saturation

The saturation region of the output of a sensor is defined as the region when the output does not respond to any change in the input even if the sensor input has linear characteristics (Fig. 2.9). The saturation is thus often considered as the limit of all sensors’ performance [15].

![Figure 2.9: Linear and saturation response regions [15].](image)

2.4.6 Calibration

The calibration of any sensor is very substantial to maintain the reliability of the measurements. Each kind of sensor has a unique limit of calibration. Fundamentally, the calibration process has to be done in the same environment where the sensor is supposed to be functioning in order to collect an accurate result. Typically, the calibration process starts with applying an input \(x\), and then plotting the output response of the sensor \(y\), corrected for an initial signal \(y_0\) against the value of the input \(x\) or \(\log(x/x_0)\), where \(x_0\) is the reference of the input [14].
2.4.7 Hysteresis

Hysteresis means that the output signal does not return to the same value when the input stimulus is increased or decreased. Therefore, the hysteresis is defined as the width of the error in terms of the measurand quantity [4]. A typical hysteresis curve is illustrated in Fig. 2.10. It is worth mentioning that it matters when approaching a fixed input value from a higher or a lower value, because in each situation the output will be different. It is obvious in the figure that there is an error due to hysteresis, which depends on the immediately preceding value [2].

![Hysteresis curve response](image)

**Figure 2.10: Hysteresis curve response [2].**

2.4.8 Dynamic Range or Span

Sensors are intended to execute over a particular range. The range of operation for a sensor from the minimum value to the maximum value is called the dynamic range as shown in Eq. (6) [14].

\[ R_{dyn} = y_{max} - y_{min} \]  

(6)

Where \( R_{dyn} \) is the dynamic range of a sensor. \( y_{max} \) and \( y_{min} \) are the maximum and minimum input signals of the same sensor respectively.

The meaningful readings will be in this range of input signals; otherwise the readings will be considered as erroneous, invalid and may affect the sensor system [14].
2.5 Summary

In this chapter, an introduction to sensors along with a brief definition of the sensing systems has been discussed. A summarized explanation of the different types of sensors was presented and different sensors characteristics were discussed based on the behavior of different sensors. In the next chapter, the background of printed electronics and their role in developing the sensor technology will be discussed.
2.6 References


CHAPTER III

INTRODUCTION TO PRINTING TECHNIQUES

3.1 Introduction

In recent years, printed electronics (PE) have received an increasing interest and development focus based on the valuable advantages that it enables; such as the capability to fabricate devices that are flexible and relatively cost efficient due to roll-to-roll manufacturing processes [1,2].

Printing is a form of manufacturing process that is used to transfer the ink onto a substrate, such as printable paper or polymer sheet by contact or non-contact methods. Depending on the application that needs the ability of folding, bending or stretching, the printed and flexible devices can be manufactured to match the requirement [3]. After determining the broader applications of printing techniques in electronics, researchers have faced new challenges and possibilities exploring new materials processing to develop sensors [4].

There are several examples of applications that have been implemented using PE technology, such as the large screen television, well-known for its lightweight and minimal thickness. It is made of self-light-emitting organic diodes with an active matrix back plane created by organic transistors with metallic nano-ink circuits. Another example is the printed solar cell that is made of thin-film inorganic materials such as copper–indium–gallium–selenium (CIGS) which can be directly mounted on the roof of a home unlike the traditional solar cell [5].

3.2 Types of Printing Techniques

There are four types of printing techniques used for PE in terms of the action of the image carrier that is responsible of the image production, gravure [6], inkjet [7], screen printing [8] and flexography [9]. Depending on the application and the nature of the product, the appropriate printing technique choice can be made, in terms of the ink,
substrate, pattern geometry, manufacturing speed, production cost, and device structure [5]. Table 3.1 illustrates the four printing techniques along with some of their characteristics [10].

### Table 3.1 Characteristics of various printed techniques (updated from [10]).

<table>
<thead>
<tr>
<th></th>
<th>Printing Speeds (ft/min)</th>
<th>Viscosity (Ps.s)</th>
<th>Ink Film Thickness (µm)</th>
<th>Lateral Resolution (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravure</td>
<td>1500-3000</td>
<td>0.05-0.2</td>
<td>0.5-8</td>
<td>15</td>
</tr>
<tr>
<td>Inkjet</td>
<td>500 (for 600x600 dpi)</td>
<td>0.001-0.04</td>
<td>0.05-0.5</td>
<td>20</td>
</tr>
<tr>
<td>Flat Bed Screen</td>
<td>300-500</td>
<td>0.5-50</td>
<td>3-60</td>
<td>15</td>
</tr>
<tr>
<td>Flexography</td>
<td>300-1000</td>
<td>0.05-0.5</td>
<td>0.5-2</td>
<td>15</td>
</tr>
</tbody>
</table>

#### 3.2.1 Gravure Printing

Gravure printing is one of the printing technologies that offers high quality printing at high speeds which makes it a very favorable process for the manufacture of electronics.

The gravure printing technique is based on the transfer of the liquid ink from the cells of an engraved cylinder to the substrate by the impact of the pressure of a rubber cylinder [11,12]. The mechanism of gravure printing is illustrated in Fig. 3.1 [14]. The doctor blade is usually made of steel and its purpose is to remove the excess ink that is applied on the engraved image roll. During the printing process, the transfer roll transfers the ink on the substrate by applying pressure.

To obtain good print, there are multiple properties that are involved such as the impression speed and pressure as well as the doctor blade angle and pressure. In addition, the substrate and ink have a substantial impact on the printing quality such as the substrate smoothness, wettability and porosity as well as the ink viscosity [13].
3.2.2 Inkjet Printing

Inkjet printing is a material-efficient process for additive production of electronics. This additive process has several benefits that have made it more desired than the other fabrication techniques, especially in that it does not require a cleanroom environment or generate any chemical waste [15]. The inkjet process depends on a deposition operation based on the ejection of picoliter droplets of the ink on the substrate using a nozzle that is movable over the substrate which allows non-contact patterning [16].

Inkjet printers can be divided into two kinds based on the deposition method: continuous and drop-on-demand, as shown in Fig. 3.2. The continuous printer relies on ink-streaming by a high voltage source. The charged droplets of ink get deflected and the non-deflected droplets are transported to the substrate. The drop-on-demand printer relies on either a piezoelectric method or thermal method that deposits the ink droplets only over the patterned area [17].

Figure 3.1: Gravure printing [14].
Figure 3.2: Inkjet technologies; (a) continuous inkjet and (b) drop-on-demand inkjet [17].

3.2.3 Screen Printing

Screen printing is a printing process that employs an image carrier with an open image area and a closed non-image area. The essential strength of screen printing is the practical ability of printing on any surface such as paper, plastic, textile and paperboard, that has enabled its widespread usage in multiple products [18]. In addition, the screen printing technique is typically used with highly viscous inks.

A typical screen printer has six components: stencil, screen frame, squeegee, screen fabric, substrate and ink, as shown in Fig. 3.3 [19,20]. Every component has a special role in the printing process. The stencil, frame and fabric jointly form the image carrier, while the squeegee forces the ink onto the substrate through the image carrier.
Figure 3.3: Schematic of the screen printing process [19].

3.2.4 Flexographic Printing

Flexographic printing is a roll-to-roll method which involves a plate cylinder that is made of photopolymers or rubber, an impression cylinder, inking unit and an anilox roll [21]. Figure 3.4 shows the mechanism of flexographic printing. An anilox roll transfers the ink to the surface of a printing plate, which has raised areas that accept ink. Subsequently, ink will be transferred from the plate to the substrate due to the pressure of the impression cylinder. A reversed angle doctor blade wipes the anilox roller, depositing the appropriate amount of ink inside the cells. The depth, shape and angle of the cells affect the ink deposition and the quality of printing [17,19].
3.3 Why Gravure Printing?

There are multiple characteristics of gravure printing that offer many significant advantages over other printing technologies such as the high velocity printing, low viscosity inks, high resolution and numerous ink film thicknesses that give a high quality printing. Gravure printing offers various advantages that allow a very efficient and high speed process to transfer the ink to the flexible substrate, and cover the complete printing area without alteration [17,22].

3.4 Summary

In this chapter, the different printed techniques and their working principles have been discussed, along with the important parameters that affect the selection of a
particular printing technology. The multiple advantages of selecting gravure printing technology was demonstrated as well.
3.5 References


CHAPTER IV
RAMAN SCATTERING

4.1 Introduction

Raman scattering is based on the inelastic scattering of light that occurs as a result of the interaction of a laser source with the vibration modes of the target molecules [1]. This interaction causes a frequency shift between the incident and scattered photons that is related to the molecular vibration energy [2]. The Raman spectrum from the target molecule provides a structurally unique fingerprint of the molecule, and therefore Raman spectroscopy is widely used as a detection and identification method for molecules [1,2].

The signal from the Raman scattering is typically weak and is known to be enhanced by the use of metallic nanostructured surface modification [3]. The interaction of the light with the metallic molecules causes a Plasmon resonance, which plays a major role in enhancing the Raman signal. Gold (Au) and silver (Ag) are examples of the metallic materials that have good optical properties and provide a high Plasmonic resonance [2]. The nanostructures of Surface Enhanced Raman Spectroscopy (SERS) have been found to present better enhancement than larger structures. While there is no limit how small the SERS structure could be, there is a requirement to have dimensions that are smaller than the source light dimensions (source light wavelength) which inherently involves nano technology. In addition, roughened metallic surfaces have been shown to provide a larger electromagnetic field when compared with flat metallic surfaces. Therefore, they roughened metallic nanostructured surface modification are considered optimum substrates to obtain a high intensity of the Raman scattered signal [2,3].

SERS provides many advantages; including, the acquisition of the Raman spectra in a relatively short period of time and its ability to collect and analyze the analyte spectra without the need of sample modification [1]. The label free usage of Raman spectroscopy and the provision of the unique fingerprints for multiple materials have made it a favorable and widely used method for identification of different types of materials. In this chapter, the basic principle of Raman scattering will be discussed along with the
definitions of Raman spectra and Raman shifts, as well as SERS methods, parameters and the enhancement factor.

4.2 Raman Scattering Theory

4.2.1 Theory of Scattering

Light scattering is defined as the interaction between the target molecules and the incident light which results in a scattered photon [3]. The scattering process is categorized into two types: elastic scattering and inelastic scattering. Elastic scattering or Rayleigh scattering occurs when the scattered photon and absorbed photon have the same energy level and wavelength [1].

Inelastic scattering occurs when there is a frequency shift between the incident and scattered photons because energy will be transferred either from the incident photon to the molecule or from the molecule to the scattered photon; consequently, there are two types of the inelastic scattering, referred to as Stokes scattering and anti-Stokes scattering [2]. Raman scattering is based on the inelastic scattering of light to identify a molecule’s structure [3]. Raman scattering starts with exciting the sample by applying a single frequency of radiation and then detecting the radiation from the sample. During the excitation process, the incident light interacts with the molecule and alters the electrons around the nuclei. This generates a virtual and unstable state in the nuclei that leads to the immediate re-radiation of the incident light.

The general scattering process of Raman and Rayleigh scatterings are demonstrated in Fig. 4.1. Typically, at room temperature most of the molecules exist in the lowest vibrational energy states (L). Consequently, when the molecule is promoted to a higher vibrational energy state (H), the scattering process is called Stokes scattering. In some cases, when the molecule exists in the highest energy state (H), and is transferred to the lowest energy state (L), the scattering process is called anti-Stokes scattering [1-3].
Figure 4.1: Rayleigh scattering, Stokes and anti-Stokes scattering [1].

4.2.2 Raman Shift

The Raman shift is defined as the energy difference between the incident and scattered photons during scattering, and it provides a fingerprint of a bio-chemical substances [1]. The Raman shift is a function of Raman intensity, which is dependent on the incident wavelength, computed as the wavenumber in units of (cm$^{-1}$). The Raman shift depends on the type of Raman scattering: it is positive for Stokes scattering and negative for anti-Stokes scattering [2].

Figure 4.2 shows the Raman spectrum of carbon nanotubes (CNT) to illustrate Raman peaks that correspond to the vibrational modes of the molecules [4]. The peaks that are shown in the Raman spectra represent the vibrational modes of the molecule and these peaks are unique for each material [5].
Figure 4.2: Example of Raman peaks for CNT [4].

4.3 Surfac ed Enhanced Raman Spectroscopy (SERS)

In 1974 Fleischmann, Hendra and McQuillan demonstrated the significant amplification in the Raman Spectra of pyridine in the presence of rough silver electrodes [1,6]. Later reports by JeanMaire, Van Duyne, Albrecht and Creighton explained that a huge enhancement in intensity of the Raman signal was observed based on the formation of special areas called hot spots, located on the boundaries of metal nanoparticles that cause an enhancement of the electromagnetic field [2]. The presence of weak signals, which is the single weakness associated with Raman scattering, was thereby overcome by the fabrication of a SERS. In application, SERS based devices are able to enhance the Raman signal up to several orders of magnitude. The principle of SERS has been based on two methods: electromagnetic enhancement and chemical enhancement [1], which will be discussed in detail in the next sections.

4.3.1 Chemical Enhancement

The chemical enhancement in Raman spectroscopy can be explained as a charge transfer mechanism when the analyte or target molecules is attached to the metallic surface chemically [1,2]. There is still much controversy about the amount of
contribution of the chemical effect to enhance the Raman signal. Most of the studies had shown a higher contribution caused by the electromagnetic effect rather than the chemical effect [1-3].

4.3.2 Electromagnetic Enhancement

Raman scattering mainly depends on the inelastic scattering of the incident photons that lead to a frequency shift of the electromagnetic field [7]. The Raman signal intensity is a function of the electromagnetic field of an analyte that is mathematically shown in Eq. (1) [8]:

$$I \alpha E_a^2$$

(1)

Where $I$ is the intensity of Raman field and $E_a$ is electromagnetic field of an analyte.

The electromagnetic enhancement occurs due to electromagnetic interaction between the incident light and metal due to the Plasmon resonance [9]. Plasmon resonance of metallic nanoparticles creates an optical frequency field, which generates the electromagnetic field that in turn results in the enhancement of the Raman signal. One of the most important requirements for obtaining this enhancement is the closeness of the molecules to the metal surface. The deposition of metal nanoparticles on a specific substrate is not uniform and this produces a diverse electromagnetic field on the surface based on the location of the nanoparticles. The highest electromagnetic fields are generated on the boundaries between the nanoparticles, which are called hot spots as illustrated in Fig. 4.3 [10,11].

Hot spots are the places where the analyte molecules settle, which causes spatial surface plasmon resonances due to the effect of the laser electric field to enhance the intensity of Raman signal that is mathematically described by Eq. (2) [12]:

$$I \alpha (E_a + E_p)^2$$

(2)

Where $E_a$ is the electromagnetic field of the analyte. $E_p$ is the electromagnetic field caused by the presence of metal nanoparticles.
During the scattering of the incident light, the vibrational transition mostly occurs from the lowest vibrational energy levels (n=0) to the next higher level (n=1), which causes strong Raman modes or infrared (IR) that are called “fundamental bands”. On the other hand, if the transition occurs to a higher level (n=>2), much weaker Raman mode or IR will be observed and are called “overtone band” [1,13]. Based on the symmetry of molecule, researchers have explained Raman active and inactive modes of the vibrational modes of the molecule [14]. Raman inactive modes occur when the incident light may not be able to produce a transition between different levels of vibrational modes because of the effect of the symmetry. It also has to be mentioned that some of the active modes present the same Raman peaks because they have the same arrangement between the vibrational levels [14].

4.3.3 Enhancement Factor (EF)

The enhancement factor (EF) in Raman spectroscopy is defined as the comparison between the intensity of Raman peaks of the target molecule obtained with and without the presence of the metallic nanoparticles, under similar test conditions [2].

There are four different methods to calculate the EF: (1) Single molecule EF (2) SERS substrate EF (3) Analytical EF and (4) Estimated EF based on the cross-section measurements [15,16]. This EF is dependent on different parameters, such as the characteristics of the incident light, molecule numbers that are contributing to the process, orientation of the analyte on the substrate, analyte absorption properties, different forms of substrates and the spectroscopy settings. In this work, the author used the SERS substrate EF calculation method that provides a comparison between the
intensities of different substrate and calculates the average enhancement mathematically by using Eq. (3):

\[ EF = \frac{I_{\text{SERS}}/N_{\text{Surf}}}{I_{\text{RS}}/N_{\text{vol}}} \] (3)

Where \( N_{\text{Surf}} \) is the average number of adsorbed molecules under SERS measurements, and \( N_{\text{vol}} \) is the average number of the scattered molecules for the Raman spectrum [1,6]. Determining the number of molecules that contribute to the production of the Raman spectra is complicated and not easy to find, therefore researchers typically estimate the number of the molecules. However, if the substrate characteristics are known, an accurate \( N_{\text{Surf}} \) and \( N_{\text{vol}} \) can be defined to identify the SERS substrate EF (SSEF) in terms of the experimentally measured spectrum [7].

### 4.4 Important Parameters for SERS

#### 4.4.1 Substrate

The perfect SERS substrate is the one that provides a significant, strong Plasmon resonance in order to enhance the weak Raman spectrum signal. The enhancement from the SERS substrate is variable, it could be uniform or have a large variation. The enhancement depends on the metallic surface due to the optical properties that are present in metals such as gold, silver, copper and platinum [17,18]. Gold and silver are commonly used in the fabrication of SERS substrates for their strong Plasmon resonance in the visible or near infrared range that produces a good enhancement when compared to other metals [17].

The metallic substrates are constructed in one of three ways: (1) Metallic electrodes; (2) A planar metallic structure, which is basically a nanoparticle array on a glass or silicon base; or (3) Metallic particle based solutions such as colloidal solutions [17]. The discovery of the metallic electrodes had an important role in the development of SERS process, especially when they are fabricated on a flexible structure by using one of the printing technologies [18]. Even though, planar metallic structures have produced a
high enhancement in Raman signal, it is typically used on a glass or silicon substrate that makes it rigid [1]. In addition, the metallic particle based solutions are commonly used in detecting molecules in a liquid mixture, in the presence of interfering molecules [1,2].

4.4.2 Analyte (Probe)

The selection of the appropriate probe for Raman spectra is one of the most important factors for the enhancement of the Raman signal. Therefore, molecules that have an electromagnetic field relative to the exciting laser source are considered as perfect candidates to be a SERS probe [19].

4.4.3 Surface Plasmon Resonance

Surface Plasmon resonance is defined as a property of metals that produces electromagnetic fields from the interaction of the metal with incident light [1,20]. Generally, metals have the capability of reflecting light in addition to their conductivity. These properties come from the existence of the free electrons in the conduction layer of metals that release energy and enhance Raman spectra. These unique properties enable the analysis of the optical characterization of metals through their dielectric function [1,2].

The dielectric function describes the electromagnetic modes of the molecules that resonate with incident light. An optimum metal that can be used in SERS should have two basic properties: (1) The real fraction of the dielectric function is large in magnitude and negative, and (2) the imaginary fraction of the dielectric function is small in magnitude. Figure 4.4 shows the dielectric function of silver (Ag) and gold (Au) with their real and imaginary parts [19].
Figure 4.4: The real and imaginary parts of the two most used metals in SERS; silver and gold [19].

4.5 Application of SERS

SERS has been used in different applications such as gemology, heavy metal detection, medical analytics and drug detection [7,12,13]. In this work, SERS has been used to detect one of the most commonly used illicit drugs, Cocaine. Drug-use continues to extract a significant toll, with precious human lives and productive years of many individuals being lost. In addition, crime records indicate that most cases involving drugs addicts often affect innocent people [21]. Using SERS as an analytical tool for the detection of drugs is promising because of its high sensitivity, selectivity and capability to provide the unique drug fingerprints.

4.6 Summary

In this chapter, the Raman scattering theory as well as the SERS mechanism has been discussed. The different principles of Raman enhancement along with the most important parameters have been presented. There are multiple technologies that are used
in fabricating SERS substrates. In the following chapter, a gravure printed silver nanoparticle based SERS substrate will be presented for the detection of cocaine.
4.7 References


CHAPTER V
DETECTION OF COCAINE USING GRAVURE PRINTED SILVER NANOPARTICLE BASED SERS SUBSTRATE

5.1 Introduction

The unprecedented phenomenon of the prevalent use of drugs of abuse, such as cocaine, in the neoteric world is closely associated with an increase in crime and violence. The widespread use of illicit drugs is also a threat to public health, specifically the youth, and ultimately the security and stability of countries [1]. The detection and identification of illicit drugs thus have a very important role in both the forensic and security contexts. Among the several techniques that have been developed for the detection of illegal drugs, Raman spectroscopy based optical detection has been widely employed as a qualitative and quantitative analysis method [2]. Research has shown that Raman spectroscopy is a reliable, rapid and non-destructive technique for analysis of different materials including drugs of abuse and illicit substances [3].

Raman spectroscopy is known to provide molecular level fingerprints that can be applied to any optically accessible sample (solid, liquid or gaseous). Raman spectroscopy is an instantaneous operation that involves either energy loss or gain from the target molecule. When a monochromatic light is applied, some of the light passes through the sample, absorbs into the sample or is reflected back from the sample depending on the nature of the material that is being analyzed and also the wavelength of the applied light. The back scattered light from the sample demonstrates the energy shift of the sample molecule. Thus, Raman spectroscopy explores the vibrational modes of the sample molecules, which can be considered as the fingerprint signal that identifies the sample material [4].

Generally, the detected Raman spectrum of many materials is weak. This is especially true for samples that are a mixture of materials, because the number of
scattered photons is insufficient and produces a low efficiency [5]. In the last decade, research has focused on enhancing the intensity of the Raman spectra by utilizing nanoscale metallic surfaces; this phenomenon is called surface enhanced Raman spectroscopy (SERS). SERS uses topically enhanced electromagnetic fields from metallic nanostructures to enhance the Raman spectra of target molecules [6,7]. SERS provides a sensitive and selective analytical detection method for bio-chemical sensing without the need of any sample preparation [8].

Several methods have been used to deposit thin metallic films for the SERS substrates fabrication such as wet chemical fabrication [9] and physical vapor deposition [10]. The most effective materials used for the deposition of the thin films are metallic nanoparticles made of gold, silver and copper [11-13]. However, these substrates are often fabricated on rigid substrates. The use of additive printing processes enables the cost efficient development of SERS substrates on flexible substrates with reduced material wastage, at room temperature [14,15].

In this work, the author has developed a novel SERS substrate, which is fabricated by gravure printing a silver nanoparticle (Ag NP) ink film on a flexible and stretchable thermoplastic polyurethane (TPU) substrate for the detection of cocaine. A thin film of Ag NP ink, with average particle size of 150 nm, is printed as the metallizing layer on a TPU substrate. The capability of the printed substrate to enhance the Raman spectra of cocaine was investigated by the author.

5.2 Metal Surface Plasmons

The surface plasmons are collective oscillations of conductive metal electrons against the background of ionic metal cores [16,17]. When the exciting laser light is resonant with the dipolar plasmon, the metal particle will radiate the characteristic of the dipolar radiation [18]. Generally, the phenomenon of the light scattering can provide a qualitative understanding of the SERS process. The incident light beam induces an oscillation dipole, $\mu$, in a particle that scatters the light at the frequency of the dipole oscillation. From different harmonic frequency components, the dipole moment and each component can be mathematically given using Eq. (1) [19]:
\[ \mu(t) = \mu^\circ \cos(2\pi vt) \]  
(1)

Where \( \nu \) is the dipole scattering frequency, and \( \mu^\circ \) in the maximum induced dipole moment for a given frequency component of \( \mu \). The induced dipole moment is given by Eq. (2) [19]:

\[ \mu(t) = P \cdot E_{inc}(t) \]  
(2)

Where \( P \) is the polarizability of the molecule. \( E_{inc} \) is the electromagnetic field generated by the interaction between the incident light and the target molecule.

The polarizability is a tensor quantity, which can be defined as the ease with which molecular orbitals are deformed by the presence of an external field. Raman intensity is proportional to the square of the induced dipole \( \mu \), thus the enhancement effect can affect the electric field experienced by the molecule that results in an electromagnetic effect (field effect) in which the molecule faces large local fields caused by the electromagnetic resonances generated on the surface of metal structures [19].

5.3 Experimental

5.3.1 Chemicals and Materials

The author used a flexible and stretchable TPU film from Bemis Associates as the substrate. Ag NP ink, with average particle size of 150 nm from InkTec Inc., was used for the metallization of the SERS substrate. Cocaine (C-008), in acetonitrile solvent, from Sigma Aldrich Chemical Co. was used as the test analyte.

5.3.2 SERS Platform Fabrication Process

The SERS substrate was fabricated using a laboratory scale gravure press (K-Printing Proofer) from Testing Machines Inc. A single layer of the Ag NP based ink, with dimension of 1.5 x 1.5 inches, was printed on the TPU substrate. The printed sample was then cured in a VWR 1320 temperature controlled oven for 15 minutes at 120 °C to form the final SERS substrate (Fig. 5.1). The printed sample was characterized using a Bruker vertical scanning interferometer microscope (CounterGT). An average thickness and roughness of 7.78 \( \mu \)m and 0.18 \( \mu \)m, respectively was obtained for the printed Ag NP metal layer as shown in Figure 5.2.
Figure 5.1: Gravure printed SERS.

Figure 5.2: 3D Profilometry scan of the printed SERS substrate illustrating (a) an average thickness of 7.78 μm and (b) an average roughness of 0.18 μm.
5.3.3 Experimental Setup

The experiment setup is shown in Fig. 5.3. 100 µl of the cocaine solution was deposited, using a pipette on a bare TPU substrate and the printed SERS substrate. The sample was left undisturbed for 5 minutes to allow for the complete evaporation of the acetonitrile solvent. The SERS measurements were performed by using a collimated diode laser system, in the near infrared region (785 nm), for exciting the samples with an integration time of 2 seconds at 300 mW. The sample was excited through the excitation fiber of a Raman probe (Inphotonics Inc.) and the Raman spectrum was collected through the collection fiber. A spectrometer (QE 65000 Ocean Optics, 780 nm – 1100 nm) was used for recording the spectra and the Spectra Suite software (Ocean Optics) was used for analyzing the Raman spectrum of the analyte under test.

**Figure 5.3: Experiment setup.**
5.4 Results

Initially, the Raman spectrum of cocaine on the bare TPU substrate was measured, as a reference signal. Then, the Raman spectrum of cocaine on the Ag NP printed SERS substrate was measured, under similar environmental conditions. Both measurements were performed with room-temperature dried cocaine to avoid the distortion and distribution of the Raman spectra caused by the acetonitrile solvent. Figure 5.4 shows the Raman spectrum of cocaine on the bare TPU substrate and the printed SERS substrate. Raman peaks at 1342.76 cm\(^{-1}\) and 1492.92 cm\(^{-1}\) were related to cocaine on the Ag NP printed SERS substrate.

An enhancement factor (EF) of the Raman spectrum, which is the ratiometric relationship of the spectral intensity between the enhanced and non-enhanced signals, can be mathematically calculated using the analytical expression Eq. (3) [20]:

\[
EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{RS}}
\]  

(3)

Where \(I_{SERS}\) is the intensity for the surface enhanced Raman spectroscopy, \(I_{RS}\) is the intensity for the normal Raman spectroscopy, \(N_{SERS}\) and \(N_{RS}\) are the number of the probe molecules in surface enhanced Raman spectroscopy and normal Raman spectroscopy, respectively. Since the same analyte was deposited on both the bare TPU substrate and the printed SERS substrate, the number of the probe molecules is equal. Eq. (3) can thus be rewritten as Eq. (4):

\[
EF = \frac{I_{SERS}}{I_{RS}}
\]  

(4)

An EF of 3 was calculated for the cocaine on the printed SERS substrate. This enhancement can be attributed to the effect of plasmonic resonance that is caused by the interaction of the metallic surface with light [21]. Electromagnetic fields are created by the existence of free electrons in the conduction layer of the metallic layer. The non-uniformity of the Ag NPs increases the electromagnetic fields at different locations which are known as hot spots. The highest enhancement in Raman spectrum is obtained from the electromagnetic field at these hot spots [22,23].
In this work, the author successfully fabricated a SERS substrate by gravure printing a AgNP ink, with average particle size of 150 nm, on flexible and stretchable TPU substrate. The feasibility of the printed device to be used as a SERS substrate was demonstrated. An EF of three was obtained for the Raman spectrum of cocaine on the printed SERS substrate, when compared to the Raman spectrum obtained for cocaine on bare TPU substrate. The impact of a stretchable substrate on the SERS response will be demonstrated in the following chapter.

Figure 5.4: Raman spectra obtained on the bare TPU substrate and the printed SERS substrate.

5.5 Summary

In this work, the author successfully fabricated a SERS substrate by gravure printing a AgNP ink, with average particle size of 150 nm, on flexible and stretchable TPU substrate. The feasibility of the printed device to be used as a SERS substrate was demonstrated. An EF of three was obtained for the Raman spectrum of cocaine on the printed SERS substrate, when compared to the Raman spectrum obtained for cocaine on bare TPU substrate. The impact of a stretchable substrate on the SERS response will be demonstrated in the following chapter.
5.6 References


CHAPTER VI

FABRICATION OF A WRINKLED NANOSTRUCTURE BASED SERS SUBSTRATE TO ENHANCE THE RAMAN SPECTRUM OF COCAINE

6.1 Introduction

Raman spectroscopy is a technique that is used for the detection of different biochemicals including drugs of abuse because of its capability to perform the analysis in a rapid, reliable and non-destructive technique [1]. The weak signal for the Raman spectra has been one of the major challenges that researchers have been dealing with for many years, especially when the test samples contain a mix of different and/or interfering biochemicals [2]. SERS is focused on enhancing the Raman signal intensity by utilizing nanoscale metallic surfaces and this enhancement effect is based on an increase in the topical electromagnetic fields from the metal nanostructures [3,4].

Generally, the use of metal nanoparticles has shown a strong effect in enhancing the Raman spectra [3]. For detection and identification purposes, a much stronger enhancement in Raman signal is required, therefore aggregation of the metal nanoparticles is very essential because both the theoretical and experimental results have indicated that an intense enhancement effect will be generated when the aggregation of two or multiple nanoparticles occurred due to the coupling of the electromagnetic field [5,6]. The Raman signal intensity can be amplified dramatically by surface plasmonics of the nanostructured metals, especially at hot spots which are locations where comparatively larger electromagnetic fields are generated in the narrow nanogaps between sharp corners and edges of nanostructured metal surfaces [7].

6.2 Theory of Metal Nanoparticle Aggregation for SERS

The Localized Surface Plasmon Resonance (LSPR) occurs due to the effect of resonance created by the collective oscillation of valence electrons on the surface of metal nanostructures and is dependent on the frequency of the incident light [8]. For the
electric field around the nanoparticle to be uniform, a quasi-static approach is considered where a spherical silver nanoparticle of radius $\sigma$ is irradiated by a polarized light $z$ of a larger wavelength $\lambda$ within the long wavelength limit of $\sigma/\lambda < 0.1$ [8-10]. In this project, the author used a AgNP ink, with average particle size of 150 nm (radius of 75 nm), and a laser source with wavelength of 785 nm. Therefore, based on the quasi-static approach, the long wavelength limit of the AgNP is calculated using Eq. (1) [10].

$$\text{Long Wavelength Limit} = \frac{\sigma}{\lambda} = \frac{75}{785} = 0.09$$  

From this result, the author concluded that the electric field generated outside the particle is uniform. This also allows for the replacement of the Maxwell’s equations by the Laplace equation of electrostatics, which is beneficial for predicting the characteristics of the SERS electromagnetic field [8,9]. The analytical solution for the magnitude of the electromagnetic field outside the particle $E_{out}$, is thus given by Eq. (2) [10]:

$$E_{out} (x, y, z) = E_0 \hat{z} - \alpha E_0 \left[ \frac{2}{D^2} - \frac{3z}{D^5} (x\hat{x} + y\hat{y} + z\hat{z}) \right]$$  

Where $x, y$ and $z$ are the Cartesian coordinates; $D$ is the radial distance between the nanoparticles; $\hat{x}, \hat{y}$ and $\hat{z}$ are the Cartesian unit vectors; and $\alpha$ is the metal polarizability expressed in Eq. (3) [10]:

$$\alpha = g\sigma^3$$  

Where $\sigma$ is the radius of the particle and $g$ is given in Eq. (4) [10]:

$$g = \frac{\varepsilon_{in}-\varepsilon_{out}}{\varepsilon_{in}+2\varepsilon_{out}}$$  

Where $\varepsilon_{in}$ is the dielectric constant of the metal nanoparticle, and $\varepsilon_{out}$ is the dielectric constant of the external environment [10]. Therefore, the electromagnetic field generated outside the nanoparticles, specifically on the narrow boundaries between the nanoparticles, is dependent on the distance between the particles. Typically, when the distance between the nanoparticles decreases, the generated electromagnetic field strength increases as a result of the LSPR. This phenomenon leads to an enhancement in the Raman spectrum intensity of the target molecule. Therefore, as discussed previously
in Chapter 4, the Raman signal intensity is dependent on and is directly proportional to the electromagnetic field as given in Eq. (5) [11]:

\[ I \propto E_{out}^2 \]  

(5)

Based on this theory, the author has designed a wrinkled AgNP based structure that will enable the aggregation of the metal nanoparticles. This aggregation will thus result in decreasing the distance between the particles and, in turn, enhance the Raman signal intensity for cocaine detection.

Figure 6.1 shows a schematic of a wrinkled surface [12]. Substantially, there are two parameters that capture the central aspects of surface wrinkling: (a) the wavelength (D) of the wrinkle; and (b) the amplitude (A) of the wrinkle as a function of strain (\( \varepsilon \)) [13,14]. The wavelength of the wrinkle pattern is linearly dependent on the thickness of the ink film as expressed in Eq. (6) [13,15]:

\[ D = 2\pi h \left[ \frac{(1-v_f^2)E_f}{3(1-v_f^2)E_s} \right]^{1/3} \]  

(6)

Where \( h \) is the thickness of the ink film, \( E \) is Young’s modulus, and \( v \) is the Poisson’s ratio for both the substrate (s) and ink film (f), respectively.

![Figure 6.1: Wrinkled structure surface [14].](image)

The amplitude of the wrinkle is also linearly dependent on the thickness of the ink film and the strain as illustrated in Eq. (7) [12].

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\[ A = h \sqrt{\frac{\varepsilon - \varepsilon_c}{\varepsilon_c}} \]  

(7)

Where the critical strain \( \varepsilon_c \) is described by Eq. (8) [15,16]:

\[ \varepsilon_c = -\frac{1}{4} \left( \frac{3E_s}{E_f} \right)^{2/3} \]  

(8)

This relation indicates that the wrinkle periodicity is proportional to the Young’s modulus \( E \) of the substrate raised to the 2/3 power. In addition, the amplitude of the wrinkle is represented by the roughness \( R \) of the ink film, Eq. (9) [15]:

\[ R = \frac{\sum_{i=1}^{5} y_{pi} + \sum_{i=1}^{5} y_{vi}}{5} \]  

(9)

Where \( y_{pi} \) is the number \( i \) of the highest peak along the profile, and \( y_{vi} \) is the number \( i \) of lowest valley along the profile [15].

Generally, gravure printing produces a dry film thickness ranging from 0.5-8 \( \mu \)m [17], as mentioned in Chapter Three. An analytical calculation was performed to model the different wavelengths and amplitudes for this expected print thickness range and thus predict the wrinkle topology. The calculations were performed for an estimated strain of 25% on an SERS substrate of 0.5” (W) by 3” (L). An estimated stress in the range of 0.1 mPa < \( \sigma \) < 1 mPa [18,19] is expected for the strain of 0.25 and \( \frac{L}{W} = 6 \). Arbitrary values from 0.1 mPa to 1 mPa, in steps of 0.2 mPa were chosen for the analytical calculations. The critical strain was also calculated to be in the range of 0.13 < \( \varepsilon_c \) < 0.56.

Figure 2 shows the results obtained for the analytical calculations of the different wavelengths and amplitudes. It was found that the wavelength increased with an increase in the print film thickness (Fig. 6.2(a)). In addition, the wavelength decreased with an increase in the stress. For example, a \( D \) of 45.23 \( \mu \)m and 21.67 \( \mu \)m was obtained for the minimum (0.1 mPa) and maximum (0.9 mPa) stresses, respectively with a print thickness of 5.0 \( \mu \)m. Similarly, analytical calculations for the different amplitudes showed that the amplitude increased with increase in the print film thickness and stress (Fig. 6.2(b)). For example, an \( A \) of 6.0 \( \mu \)m and 8.5 \( \mu \)m was obtained for the 0.1 mPa and 0.9 mPa, respectively with a print thickness of 5.0 \( \mu \)m. These results demonstrated that the lowest print thicknesses resulted in smallest wrinkles with lower amplitude and wavelength, which would in turn act as the best hot spots to enhance the Raman signal.
Figure 6.2: Thickness effect on the wrinkles (a) wavelength and (b) amplitude.
6.3 Chemicals and Materials

A flexible and stretchable thermoplastic polyurethane (TPU) film from Bemis Associates was used as the substrate. Polyethylene terephthalate (PET) flexible substrate was used as a supportive substrate. Ag NP ink, with average particle size of 150 nm from InkTec Inc., was used for the metallization of the SERS substrate. Cocaine (C-008), in acetonitrile solvent, and acetonitrile (360457) from Sigma Aldrich Chemical Company, were used as the analytes.

6.4 Fabrication of the Wrinkled SERS Substrate

The wrinkled AgNP based SERS substrate was designed with dimensions of 3 × 0.5 inches. The SERS substrate was fabricated by gravure printing AgNP using a K-printing proofer and the wrinkled nanostructures on the SERS substrate was formed by stretching the substrate while printing. The formation of the wrinkles on AgNP, due to the stretch and release process, will create a rougher surface resulting in an effective plasmonic substrate [7]. In order to maintain the elongation during the printing process, the TPU substrate was attached using sticky tape to a PET substrate before mounting on the gravure printer roll. The curing of the printed samples was done in two ways: (a) curing while being stretched and (b) curing without stretching. The printed sample was cured in a VWR 1320 temperature controlled oven for 5 minutes at 85 °C to form the final SERS substrate (Figure 6.3).
Figure 6.3: Image of the SERS substrate, mounted on the PET substrate.

6.5 Substrate Characterization

Figure 6.4 shows the images of the bare TPU and AgNP printed SERS substrates, both non-stretched and 25% stretched samples, taken using a SemiProbe Probe Station. The roughness of the SERS substrates was measured for a better understanding of the characteristic transformation of the substrates before and after stretching. Using a Bruker GTL-EN-61010 profilometer, the average roughness of the bare TPU substrate before and after stretching was measured to be 2.60 μm (Figure 6.5(a)) and 2.76 μm (Figure 6.5(b)), respectively. Similarly, the average roughness of the AgNP printed SERS substrate before and after stretching was measured to be 1.30 μm (Figure 6.5(c)) and 1.57 μm (Figure 6.5(d)), respectively. The roughness of the stretched SERS substrate was higher than the roughness of the non-stretched SERS substrate, which indicates the formation of the wrinkled surface [15].
Figure 6.4: Images of the: (a) bare non-stretched TPU, (b) bare 25% stretched TPU, (c) non-stretched AgNP printed SERS substrate, and (d) 25% stretched AgNP printed SERS substrate.
Figure 6.5: The 3D profilometry scan for measuring the roughness of the (a) bare non-stretched TPU, (b) bare 25% stretched TPU, (c) non-stretched AgNP printed SERS substrate, and (d) 25% stretched AgNP printed SERS substrate.
The average thickness of the ink film for the non-stretched SERS substrate was measured to be 4.3±0.2 µm (Figure 6.6(a)). The average thickness of the 25% stretched SERS substrate was measured to be 5.3±1.7 µm (Figure 6.6(b)). It was observed that the thickness of the non-stretched SERS substrate was mostly uniform along the SERS substrate surface, while the thickness of the stretched SERS substrate was found to have a higher variation along the surface of the SERS substrate. This variation in the thickness of the stretched SERS substrate illustrates the variation in the wavelength of the wrinkles, where the lower thickness represents a smaller wavelength region that symbolizes the best hot spot area for generating a higher electromagnetic field to reflect the higher intensity in Raman spectrum [10,15].

Also by using a Bruker GTL-EN-61010 profilometer, the average wavelength (D) and amplitude (A) of the 25% stretched SERS substrate were measured to be equal to 30.5 µm and 3.97 µm respectively, which they are produced with a critical strain of the ink film $\varepsilon_c = 0.18$. These results are directly correlating to the analytical calculations ranges for the wavelength $13 < D < 63$ µm, amplitude $3.6 < A < 11.9$ µm, and critical strain $0.13 < \varepsilon_c < 0.56$. 
Figure 6.6: The 3D profilometry scan for measuring the thickness of the (a) non-stretched AgNP printed SERS substrate, and (b) 25% stretched AgNP printed SERS substrate.
6.6 Experimental Setup

The experiment setup is shown in Figure 6.7. 100 µl of the analyte (cocaine solution and acetonitrile) were deposited on separate SERS substrates, using a pipette on the printed SERS substrate for both the stretched and non-stretched samples. The sample was left undisturbed for 5 minutes to allow for the complete evaporation of the acetonitrile solvent. The SERS measurements were performed using a collimated diode laser system, in the near infrared region (785 nm), for exciting the samples with an integration time of 2 seconds at 300 mW. The sample was excited through the excitation fiber of a Raman probe (Inphotonics Inc.) and the Raman spectrum was collected through the collection fiber. A spectrometer (QE 65000 Ocean Optics, 780 nm – 1100 nm) was used for recording the spectra and the Spectra Suite software (Ocean Optics) was used for analyzing the Raman spectrum of the analyte under test.

Figure 6.7: Experiment setup.
6.7 Results

To the best of the author’s knowledge, the elasticity of the TPU substrate for this application has not been studied previously. Therefore, a study on the effect of stretch and release on the length of the TPU substrate for different strains (25%, 50%, 75% and 100%) was initially performed. Figure 6.8 shows the results of the elongation tests for the bare TPU substrate. The change in length for the bare TPU is calculated using Eq. (10).

\[
\text{Change in length} = \frac{\Delta L}{L} \times 100\%
\]

Where \( L \) is the initial length of the substrate, and \( \Delta L \) is the difference between the initial length of the substrate and the final length after stretching.

It was observed that there was a 6%, 16%, 20% and 23% change in length of the TPU substrate for the 25%, 50%, 75% and 100% strains, respectively. Therefore, from the elongation study, the author has concluded that the lowest elongation of 25% has the least change in length after release. Figure 6.9 shows the results of the elongation tests for the AgNP printed SERS substrates towards the 25%, 50%, 75% and 100% strains for the two different curing processes. For the printed SERS substrates that were cured with stretching, it was observed that there was a 0%, 6%, 8% and 10% change in length of the TPU substrate for the 25%, 50%, 75% and 100% strains, respectively. For the printed SERS substrates that were cured without stretching, it was observed that there was a 0%, 3%, 6% and 8% change in length of the TPU substrate for the 25%, 50%, 75% and 100% strains, respectively. The change in length after releasing for the TPU substrate is generally higher than the printed SERS substrates of both curing processes, because of the heat effect on the printed SERS substrates and also the addition of the AgNP ink film resistivity. Therefore, from the elongation study, the author has concluded that the lowest elongation of 25% has the least change in length after release, for the AgNP printed substrates.
Figure 6.8: The elongation study of the bare TPU substrate.
Figure 6.9: The elongation study for the AgNP printed SERS substrates that were: (a) kept stretched and (b) not kept stretched during the curing process.
Figure 6.10: The Raman spectrum of the AgNP printed SERS substrates under different stretching rates for: (a) samples that are kept stretched during the curing process and (b) samples that not kept stretched during the curing process.

Following this, the Raman spectra of the AgNP printed SERS substrates were measured for the 25%, 50%, 75% and 100% strains. Figure 6.10 shows the Raman spectroscopy based response of the SERS substrates towards the different strains for the two curing processes. The results demonstrated that the SERS substrates subject to the 25% strain generated the highest intensity of Raman spectra in both cases. However, the
peaks for the AgNP were more prominent in the substrates that were kept stretched during the curing process. On the other hand, the author discovered that the SERS substrates that were not kept stretched during the curing process demonstrated a higher intensity in Raman signal when compared with the substrates that were kept stretched during the curing process.

Figure 6.11 shows the Raman spectra of cocaine on the SERS substrates that were subject to the 25%, 50%, 75% and 100% strains and for the two different curing processes. The results demonstrated that the SERS substrates subject to the 25% strain generated the highest intensity of Raman spectra in both cases. It was observed that the SERS substrate that was subject to the 25% strain demonstrated the largest enhancement in the intensity of the Raman signal for cocaine. This outcome can be expected based on the results obtained from the elongation study, where it was found that the SERS substrate with the 25% strain had the least change in length after the stretch-release test (0%), as well as the higher intensity of the Raman signal when compared to the non-stretched SERS substrate, during both the two different curing processes. The response of the other strains (50%, 75% and 100%) is also enhanced when compared with the non-stretched SERS substrate because the wrinkled surface was formed also for these cases but with the increment of strain the porosity of the TPU substrate increases too, thus the absorption of the TPU substrate to the AgNP ink increases. The porosity increment produces a non-perfect ink film which results a better Raman signal for the target molecule when compared with the non-stretched SERS but it is not the best.

The responses also demonstrated that the SERS substrates that were kept stretched during the curing process demonstrated a better Raman signal with relatively less noise along with sharper and more detectable Raman peaks, as shown in Fig. 6.11. On the other hand, the SERS substrates that were not kept stretched during curing process showed a high intensity in Raman spectrum of cocaine. However, the Raman signal was more distorted, due to noise, and it could be difficult to identify the Raman shifts for cocaine. This can be attributed to the fact that the wrinkled surface formation is uncontrolled during the curing process since the SERS substrate starts to regain its original form rapidly under the heat.
Finally, the author compared the intensity of the Raman signal of the cocaine solution, on the SERS substrate subject to the 25% strain, with the Raman signals of the interfering elements including the bare TPU substrate, printed AgNP on TPU substrate and acetonitrile solvent on the AgNP printed SERS substrate (Fig. 6.12). The peaks for the Raman shift of cocaine were obtained at 1268.70 cm\(^{-1}\) and 1433.43 cm\(^{-1}\) for the non-stretched SERS substrate, and at 1264.86 cm\(^{-1}\) and 1422.43 cm\(^{-1}\) for the 25% stretched SERS substrate [20,21]. The peaks for the Raman shift of the acetonitrile solvent on the AgNP printed SERS substrate were obtained at 635.11 cm\(^{-1}\) for the non-stretched SERS substrate and at 639.7 cm\(^{-1}\) for the 25% stretched SERS substrate.
Figure 6.11: The Raman spectrum of cocaine of the AgNP printed SERS substrates under different stretching rates for: (a) samples that are kept stretched during the curing process and (b) samples that not kept stretched during the curing process.
Figure 6.12: The Raman spectrum of bare TPU, Ag NP layer on TPU, Acetonitrile and Cocaine on (a) Non-stretched SERS substrate. (b) 25% stretched SERS substrate

The enhancement factor (EF) for the strongest peak of the Raman spectra of cocaine was calculated using Eq. (11) [22]:

\[
\text{EF} = \frac{I_{SERS}}{I_{bare}}
\]
where, $I_{SERS}$ is the intensity of the wrinkled SERS substrate and $I_{RS}$ is the intensity of the non-stretched SERS substrate. $N_{Surf}$ and $N_{Vol}$ are the number of the adsorbed and scattered molecules, respectively. In Eq. (11), $N_{Surf}$ and $N_{Vol}$ can be eliminated because the number of molecules of the cocaine solution are same for the adsorbed and scattered light. Therefore, an EF of 2 was calculated for the Raman shift of cocaine on the AgNP printed SERS substrate.

An EF of 6 was calculated for the Raman spectrum of cocaine on the 25% stretched SERS substrate, when compared to the Raman spectrum of cocaine on bare TPU (Fig. 6.13).

![Raman Spectrum of Cocaine on Wrinkled SERS Substrate and Bare TPU](image)

**Figure 6.13:** The Raman spectrum of cocaine on the wrinkled SERS substrate and on the bare TPU substrate.


6.8 Summary

In this chapter, the author discusses the need for the fabrication of a wrinkled nanostructure based SERS substrate that is important for drug detection applications. An analytical calculation was performed to discover the wrinkle’s topology and its relation with the printed ink film characteristics. A detailed experiment was included to select an optimum strain for creating the wrinkled nanostructure surface on the SERS substrate, and also a detailed study of two different curing process to produce an enhanced Raman signal intensity for the detection of cocaine. A novel wrinkled nanostructure was successfully fabricated by gravure printing AgNP ink on a flexible and stretchable TPU substrate. The feasibility of the fabricated substrate to enhance the Raman signal of cocaine was investigated and an EF of 2 was obtained for the Raman spectrum of cocaine on the wrinkled SERS substrate when compared to Raman spectrum of cocaine on the ordinary (non-stretched) SERS substrate. And an EF equal to 6 was obtained for the Raman spectrum of cocaine on the wrinkled SERS substrate when compared to Raman spectrum of cocaine on bare TPU substrate.
6.9 References


CHAPTER VII

CONCLUSION AND FUTURE WORK

7.1 Summary

In this thesis, the author has successfully demonstrated the development of a printed surface enhanced Raman spectroscopy (SERS) substrate, by gravure printing silver nanoparticle (AgNP) ink on a flexible and stretchable thermoplastic polyurethane (TPU) substrate for the detection of cocaine.

The author has focused on two research projects. The first project involved the development of an SERS substrate by gravure printing AgNP ink on a TPU substrate with dimensions of 1.5 × 1.5 inches. The feasibility of the printed SERS substrate for the detection of cocaine was successfully investigated and an enhancement factor (EF) of 3 was calculated for the Raman spectrum of cocaine on the printed SERS substrate when compared to the Raman spectrum of cocaine on the bare TPU substrate.

In the second project, a novel wrinkled nanostructure surface for the printed SERS substrate was developed for amplifying the Raman spectrum of cocaine for more efficient detection. The SERS substrate, with dimensions of 3 × 0.5 inches was fabricated by gravure printing AgNP ink on the stretchable TPU substrate with different strains (25%, 50%, 75% and 100%), in order to discover the best form factor that will result in an optimum wrinkled nanostructure surface. The author found that the 25% strain demonstrated the most improved Raman spectrum of cocaine with higher intensity and sharper peaks. An EF of 2 was calculated for the strongest Raman peak of cocaine on the wrinkled SERS surface when compared to the Raman peak of cocaine on the ordinary (before wrinkles formation) SERS substrate. And an EF of 6 was calculated for Raman spectrum of cocaine on the wrinkled SERS substrate when compared with the Raman spectrum of cocaine on the bare TPU substrate.

The results of this work have a significant application in developing the SERS method as a detection and identification method of cocaine and a wider range of illicit drugs and biochemical materials as well.
7.2 Future Work

The author considers this thesis work as a first step in the development of a novel SERS substrate for the detection of various bio-chemicals. The author believes that there are multiple paths that can be taken for further advancements in this field. This work has continued to inspire the author to pursue a PhD degree and continue research in developing the fabricated SERS substrate and investigate the specific characteristics and parameters of the fabricated substrate and the experimental setup to obtain the best enhancement in Raman signal.

Even though the fabricated SERS substrate was used to demonstrate the capability to detect cocaine with higher intensities, a wider variety of bio-chemicals can be investigated. For example, other illicit drugs such as heroine and methamphetamine; heavy metals such as mercury, lead and cadmium; and even explosives such as DNT and TNT.

Further studies could be performed to understand the effect of the SERS substrate response when the printed sample was not stretched during the curing process. For example, the reason behind the Raman spectrum distortion could be investigated and an algorithm could be developed to filter the noise in the Raman spectra.

In yet another approach, a study to investigate the effect of the printed design by modifying the ratio of length to width could be performed. This could lead to a rougher metal surface resulting in a more wrinkled nanostructured substrate. A stronger Raman peak could thus be obtained due to an increase in the electromagnetic field.

The use of stretchable inks instead of the more common AgNP ink could be another interesting study. In this case, the combination of the stretchable TPU substrate and stretchable ink will enable a new path that may offer more flexibility and elasticity. In addition, a more efficient stretching process of the printed SERS substrate during the printing and curing process could be obtained, which could also reduce ink film distortion.

It would also be interesting to investigate the possibility of using a different printing technology rather than gravure printing technology, such as inkjet or screen printing to
design a specific array to study the perfect and exact design that demonstrates the highest intensity in Raman signal.

7.3 Conclusion

The direct association between the use of illicit drugs and the rise of crimes and violence had been always a very important motivation to improve the detection and identification methods such as Raman spectroscopy based optical detection.

In this work, the author had developed a novel SERS substrate as a sensitive and selective analytical detection technique for cocaine by utilizing a nanoscale wrinkled metallic surface that enhanced the electromagnetic fields resulting in enhanced Raman spectrum of cocaine. The result of this work is very important in developing the Raman spectrum technique for detection and identification of cocaine and other kinds of illicit drugs.