EXPERIMENTAL AND SIMULATED STUDY OF FLEXIBLE ELECTRONICS
--FABRICATION OF WATER-SOLUBLE ZN/PVA SENSOR AND STRETCHING SIMULATION OF GNM/SWNT

A Thesis in
Engineering Science and Mechanics
by
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Flexible electronics are broadly studied for the potential in wearable devices. Transient and flexible electronics for human health monitoring are promising because this kind of electronics can be implantable and zero-waste after use. Transient electronics are commonly fabricated in the cleanroom. The process is time-consuming and costly. Photonic sintering method occurred in recent years and it provides a fast, cheap and low-temperature way of fabrication about transient electronics. This study takes advantage of photonic sintering technique to fabricate fully dissolvable PVA/Zn ECG sensor, EMG sensor and temperature sensor. Different substrates are utilized for ECG sensor and their performance are compared. The dissolution of electrodes in the water is also studied. In order to study the mechanical properties of flexible electronics, the simulation about stretching of porous graphene/carbon nanotube is also studied. The stress and strain contour of the stretched bilayer structure is obtained indicating a better tensile stiffness of the composite.
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Chapter 1 Background & introduction

1.1 Flexible electronics

Flexible electronics are a kind of electronics that can function well under folding or twisting modes. Flexible electronics are typically composed of two layers: one thin substrate and one functional electronic component. In some cases, there also exist one encapsulation layer. Flexible electronics have a wide range of applications include flexible circuit [1], flexible displays [2], flexible solar cells [3], implantable medical sensors [4] and lab-on-skin electronics [5].

Flexible electronics have advantages in lab-on-skin electronics for conformability and flexibility since human skin is soft, flexible and stretchable. Table 1 shows various kinds of lab-on-skin electronics that have different functions like sensing EEG, ECG, EMG signal, temperature, strain and hydration from human skin for better health monitoring.

<table>
<thead>
<tr>
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<th>Functions</th>
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<td>Ref. [6-8]</td>
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1.2 Transient flexible electronics

Transient electronics are a class of electronics that can dissolve into certain liquids, like biofluid or water after stable operation for a period of time. Transient and flexible electronics have specific need in temporary biomedical implants [17-20]. It can be designed as biodegradable electronics onto human body for health monitoring sensing. It can be brain sensors to measure intracranial pressure and temperature [21]. It can also work as transient spatiotemporal mapping of electrical activity from the cerebral cortex [22]. No byproduct remains and no second surgery needs for the implant transient electronics after use. Transient electronics usually consist of semiconductors, conductors, dielectrics, and substrate.

Metal layer serve as conductor and interconnection. Metals have higher electric conductivity than conductive polymer. Magnesium (Mg), Zinc (Zn), Iron (Fe), Molybdenum (Mo) and Tungsten (W) are dissolvable metals for transient electronics. Mg, Zn, Fe and Mo are micronutrients and they are important for human body[23]. Mg, Fe and their alloys can be used as bioimplants [24-26]. The dissolvable rate of different metals are different: Mg dissolves in a simulated body fluids (SBFs) at 0.05-0.5 μm/h and Fe dissolves at a rate of 0.2μm/h [23]. Dissolution rate in DI water for various kinds of metals can be found in table 2 [23]. We can observe from the table 2 that dissolution rate of Mg and Zn are quicker than the rate of W and Mn. By selection of different metals, different level of dissolution requirement can be satisfied.
Table 2. Dissolution rate in DI water for different metal material [23]

<table>
<thead>
<tr>
<th>Material</th>
<th>Dissolution rate in DI water (μm/h)</th>
<th>References</th>
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<tr>
<td>Mg</td>
<td>0.07</td>
<td>Ref. [23, 27]</td>
</tr>
<tr>
<td>Mg AZ31B alloy</td>
<td>0.02</td>
<td>Ref. [28]</td>
</tr>
<tr>
<td>Sputtered W</td>
<td>1.7x10^{-3}</td>
<td>Ref. [29]</td>
</tr>
<tr>
<td>CVD W</td>
<td>3x10^{-4}</td>
<td>Ref. [29]</td>
</tr>
<tr>
<td>Mo</td>
<td>3x10^{-4}</td>
<td>Ref. [30]</td>
</tr>
<tr>
<td>Zn</td>
<td>7x10^{-3}</td>
<td>Ref. [31]</td>
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Many water-soluble polymers contain hydrophilic groups so that they can dissolve into water. Common water-soluble substrate include poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP) and polylacticcoglycolic acid (PLGA) [18]. Polyvinyl alcohol (PVA) is a water-soluble, biodegradable and biocompatible synthetic polymer that is widely used in wound dressings, drug delivery, implants and artificial organs [32]. PVA/starch blends are widely used in packaging [33]. Figure 1.1 is the chemical structure of PVA polymer under partially hydrolyzed state and fully hydrolyzed state.

![Figure 1.1 Chemical structure of PVA: (A) partially hydrolyzed; (B) fully hydrolyzed](image-url)
For the semiconductors in transient electronics, silicon is widely used in electronic industry. Since silicon can dissolve in water through hydrolysis, monocrystalline silicon nanomembranes and silicon oxide are applied in transient electronics [34].

1.3 Photonic sintering

Photonic sintering or photonic curing is a technology that can sinter metal nanoparticles like Cu, Ag and Zn in millisecond level. The working principle is as follows: a broad-spectrum light is introduced onto the target nanoparticles and the energy of optical light converts into heat of nanoparticles. Nanoparticles then merge together to form a conductive layer. Photonic sintering has many advantages. It is a fast process that can generate conductive layer within milliseconds. Since the exposure period of light is short, photonic sintering is also a low-temperature fabrication procedure that will not damage the thermal sensitive substrate. It is also a cheap process. Large area sintering can be achieved by roll-to-roll light sintering. The broad spectrum of xenon light makes it possible to sinter a variety of nanoparticles.

In order to compare the performance of photonic sintering and thermal sintering, current collecting grids by inkjet printing for organic solar cells are sintered by thermal treatment and photonic sintering [35]. It shows that similar conductivities are achieved by 5 seconds of photonic sintering and 6 hours of thermal sintering.

Cu and Ag are commonly used in photonic sintering manufacturing process because of their good electric conductivity. Yuki Yamamoto, et al. [36]fabricated a skin temperature sensor and gel-less ECG sensor by printing Ag electrode onto PET substrate. This is a waterproof, wearable and flexible healthcare device. However, Cu and Ag are not biocompatible metals and can not be implanted into human body. Among water-soluble metals like Mg, Zn, Mo, Zinc has relative low
melting temperature (~ 420 °C) and therefore is a good candidate for photonic sintering. Bikram Kishore MAHAJAN, et al. [37] fabricated conductive zinc patterns by direct ink printing and photonic sintering. And the conductivity is improved by laser annealing approach. It also discussed the effect of the component of the ink: 0.1 wt% PVP is an optimal value to prevent Zn particles from oxidation.
Chapter 2. Fabrication method

A fully dissolvable PVA/Zn electrode is fabricated for ECG, EMG and temperature detection. The novelty of fabrication method is to sinter a layer of Zn from PI film to PVA membrane through photonic sintering process. Below are details of each fabrication step.

2.1 Preparation of PVA solution

PVA solution is prepared by mixing 10 wt% of PVA particles (Sigma-Aldrich, Mₚ 89,000) into distilling water. The solution is heat up to 90 °C by a hot plate and stirring through magnetic bar for 2 hours. Here a layer of plastic food wrap is used to seal the beaker in order to prevent water evaporation. A transparent solution can be achieved finally. Figure 2.1 shows the preparation of PVA solution. The temperature of hot plate is 92 degree and the transparent 10 wt% of PVA solution is achieved after stirring.

Figure 2.1 Preparation of PVA solution
2.2 Preparation of PVA membrane

Then we cast the PVA solution onto glass slide and use film applicator to prepare a uniform PVA membrane. It takes 1-2 hours for the solution to dry out and form PVA membrane. The PVA membrane can be easily peeled off from the glass slides. Figure 2.2 (A) is the film applicator. Figure 2.2(B) shows the wiped fabrication process for thin-film PVA membrane on glass slides.

![Film applicator and PVA membrane preparation](image)

Figure 2.2 film applicator and preparation of PVA membrane.

(A) the manual film applicator; (B) the wiped fabrication process for thin-film PVA membrane on the glass slide.

2.3 Preparation of zinc/ethanol ink

27.27 wt% of zinc/ethanol ink was prepared by directly mixing zinc nanoparticles and pure ethanol solution together. Zinc nanoparticles (Zinc, high purity, 99.9%, 35-45nm) was purchased from US Research Nanomaterials, Inc. The ink was loaded into a small glass bottle and the bottle was put...
into an ultrasonic glasses cleaner for 30-minute ultrasound oscillations. Uniform zinc/ethanol ink can be obtained after 30-minute ultrasound oscillations. Every time before the use of ink, a 30-minute ultrasound oscillation is needed. Figure 2.3 is the 27.27 wt% of zinc/ethanol ink.

Figure 2.3 zinc/ethanol ink

2.4 Preparation of Zn/PI film

Polyimide (PI) films are temporary substrates to hold a layer of zinc nanoparticles for transfer printing onto PVA membrane. The PI films have thickness of 8.47 μm and size of 1cm*1cm. We use micropipette to transfer 10 μml of zinc ink onto PI films. The PI film is pretreated by UV Ozone for 10 minutes in order to increase the uniformity of the spread ink drop. Figure 2.4 is the Digital UV Ozone system for the pretreatment of PI film. The reason to choose PI film is because of its high temperature resistance. The glass transition temperature can reach 350 °C [38]. The PI film with the thickness of 8.47 μm is the thinnest film that can be purchased in market. The thin
layer of PI film will help to improve the photonic energy that exerts onto Zn nanoparticles for transfer printing.

![UV Ozone system](image)

Figure 2.4 UV Ozone system

Figure 2.5 are the samples of dried zinc/ethanol ink on PI films. The surface of the Zinc layer become oxidized soon and therefore it is nonconductive. These samples can not be sintered directly due to the barrier of surface oxide layer. One way to solve this issue is to flip the PI film and sinter Zinc nanoparticles onto another target substrate, such as PVA membrane. The photonic energy will heat up Zinc nanoparticles and Zinc oxide layer. Due to the huge mismatch of melting temperature between Zn (419.5 °C) and ZnO (1975 °C), the Zinc particles will melt first and transfer onto target PVA membrane. ZnO will remain onto the PI film. Figure 2.6 shows the schematic illustration of transfer process.
2.5 Transfer printing of Zn/PVA membrane

Figure 2.5 Dried Zinc nanoparticles on PI films

Figure 2.6 Schematic illustration of transfer printing process
After the ink becoming dry, we will put a shadow mask and PVA membrane onto the PI film. Then the Zinc nanoparticles will be transferred to target PVA membrane from PI film by Xenon pulsed light. The reason why I did not directly coat the Zinc nanoparticles onto PVA membrane is because zinc oxide occur at the surface layer and the sintering process can not be completed. The power of Xenon light system is set as 2433J with 3000V, which the 9 J/cm^2 radiant energy is achieved (figure 2.7).

![Xenon X-1100 Photonic Sintering System](image)

**Figure 2.7 The XENON X-1100 photonic sintering system**

We can find from figure 2.8 that the maximum radiant energy (9 J/cm^2) is set under the conditions of 3000V voltage and 2433 J as energy per pulse. The starting time of pulse is 7000us and the off time of pulse is 7052 us which indicating the pulse time is 52 us.
Figure 2.8 Parameter setting screen of X-1100 photonic sintering system
Chapter 3. Results and discussion

3.1 Scanning electron microscope (SEM) images

A scanning electron microscope (SEM) is a type of electron microscope that take advantage of a focused beam of electrons to scan the surface of the target sample. The surface topography and composition can be obtained through SEM image.

Figure 3.1 SEM image of Zn nanoparticles before and after photonic sintering

The SEM image (left) shows the Zn nanoparticles on PI film before sintering. We can observe nanoparticles pile up without solid connection. The SEM image (right) shows the Zn layer onto PVA membrane. We can observe that nanoparticles merged and connected together. The scale bar is 40 μm. For a 1cm*1cm sample, the electric resistance changes from nonconductive state before sintering to 60 Ω after sintering.
Figure 3.2 SEM image of PVA membrane before and after attaching to skin

The SEM image (left) represent the flat PVA membrane. The surface is smooth before attaching to human skin. The scale bar is 200 μm. The SEM image (right) represent the PVA membrane after attaching to the skin. The partial dissolvable PVA membrane is sticky to skin with the help of small amount of water. We can find obvious skin wrinkles on the PVA membrane which indicate a good contact between the membrane and skin. Scale bar is 500 μm. The average diameter of skin patterns is around 90 μm.

3.2 Size effect of electrodes for surface electric resistance

The surface electric resistance change with the size of electrode. From the figure 3.3, we can find that the electric resistance increased linearly when the length increased. This result indicates a relatively uniform distribution of Zn metal layer after transfer sintering process.
3.3 The change of electric resistance under strain

Since the PVA/Zn membrane is very thin, it is difficult to stretch the PVA/Zn membrane directly. I used a layer of PDMS as substrate and put PVA/Zn membrane onto the PDMS substrate. A homemade extensometer is applied to stretch PDMS and PVA/Zn membrane at the same time. In order to keep good adhesion and real simulation, several drops of water are added between PDMS and PVA/Zn membrane. The increase of resistance in the figure 3.4 is because of the formation of cracks at the surface of Zn metal layer.
Figure 3.4 Electric resistance change with respect to strain

3.4 ECG signals

electrocardiogram (ECG) sensor is a basic healthcare sensor that can be used to detect electric function of the heart and it is helpful in prediction of heart diseases. The continuous measurement from ECG sensor will provide real-time feedback about cardiovascular disease to patients. As is shown in figure 3.8, an ECG signal can be separated into three main parts: The P wave, the QRS complex and the T wave. From the book [39], abnormal P,QRS or T waves represent risks of different diseases. The P wave represents the depolarization of the atria. The P wave is normally upright. The inverted P wave indicates either dextrocardia or abnormal atrial depolarization. If the P wave is too high, it indicates the right atrial enlargement. If the P wave is too wide (normally less than 0.12s duration), it may indicate left atrial enlargement [34]. The QRS complex represents the depolarization of the ventricles. If QRS complex is too wide (longer than 120ms), it suggests bundle branch block or ventricular rhythms, or hyperkalaemia. Low-amplitude QRS complex may
represent obesity, emphysema or pericardial effusion [34]. If any of R or S wave are too big, it indicates ventricular hypertrophy, posterior myocardial infarction, Wolff–Parkinson–White syndrome (left-sided accessory pathway), dextrocardia or bundle branch block [34]. The T wave represents the repolarization of the ventricles. If T wave is too tall, it suggests hypokalaemia, pericardial effusion or hypothyroidism. A reversed T wave may be caused by myocardial ischaemia, myocardial infarction, ventricular hypertrophy with ‘strain’, digoxin toxicity, pericarditis, permanent ventricular pacing, hyperventilation, mitral valve prolapse, pulmonary embolism or subarachnoid haemorrhage [34].

The key component of ECG sensor is the electrodes. One pair of electrodes can measure the potential difference between two locations of electrodes. In medical field, 10 electrodes are used to measure 12 ECG signals at different locations. Here in this study, I only measure the voltage difference between left arm wrist and right arm wrist. In order to get better ECG signal, many novel materials are applied: The graphene-based dry flexible ECG can collect data with high signal-to-noise ratio in different state of motion [40]. The liquid metal make ECG drawable [41]. ECG sensor are often combined with other sensors on skin electronics for comprehensive understanding of the health condition [42].

Figure 3.5 (A) PVA/Zn electrode for ECG sensor; (B) commercial gel electrodes
Standard wet silver/silver chloride (Ag/AgCl) gel electrodes are commercially used worldwide. However, Ag/AgCl electrodes are rigid and are uncomfortable for human skin. Flexible and wearable ECG sensor can be conformal to the human skin and they are promising for long-term sensing. The adhesion quality can be measured by the contact impedance. Low contact impedance between skin and sensor will improve the signal. Ag/AgCl electrodes need an electrolytic conductive gel to reduce the contact impedance. Here in my study, a partially water-soluble layer of PVA will provide a conformal contact between skin and sensors and therefore we can get good ECG signals compared with commercial sensors.

![Schematic circuit diagram]

Figure 3.6 Schematic demonstration of simplified equivalent circuit between the electrode and skin

The simplified equivalent circuit between the electrode and skin can be modeled as a parallel circuit of resistance and capacitance (figure 3.6), which is
\[ |Z| = \frac{1}{\sqrt{(1/R)^2 + (\omega C)^2}} \]

Larger contact area, thinner thickness of substrate and good conductivity of metal layer would reduce the impedance between skin and the sensor.

![Contact impedance change vs frequency](image)

Figure 3.7 Contact impedance change vs frequency. The red line indicates PVA/Zn electrode and the black line shows the commercial gel electrode.

In figure 3.7, the electrode-to-skin contact impedance for PVA-Zn electrode and commercial gel electrode were measured. The contact impedance is 29.4 kΩ of commercial gel electrode (area: 3.14 cm², gap distance: 1.5cm) and is 39.9 kΩ of PVA-Zn electrode (area: 1.5 cm², gap distance: 1.5cm) at 100 Hz. Although the impedance of PVA-Zn electrode is larger than commercial gel electrode, it is smaller than gel-based electrode (145 kΩ, area 3.14 cm²) and gel less sticky sensor (>1000 kΩ, area 3.14 cm²) as reported in [36].
As is shown in figure 3.8, a standard ECG signal includes P wave, QRS wave and T wave. The signal noise ratio (SNR) is calculated as

\[ SNR = 20 \log_{10} \frac{V_s}{V_n} \]

Where \( V_s \) is the peak-to-peak value of signal and \( V_n \) is the peak-to-peak value of noise. Here I followed the definition of \( V_s \) and \( V_n \) in [43]: \( V_s \) is the difference between R and S wave and \( V_n \) is the difference of the largest noise.

![Diagram of ECG signal showing P, QRS, T waves and Vs, Vn amplitudes.](image)

Figure 3.8 Demonstration of P, QRS, T wave and Vs, Vn amplitude of an ECG signal.

Figure 3.9 is the ECG signal collected by PVA/Zn electrodes (back line) and commercial gel electrodes (red line) simultaneously. From the figure, we can clearly observed that my PVA/Zn electrodes can sense the ECG signal as good a commercial gel electrodes. The SNR from PVA/ZN electrodes is 19.74 and the SNR from commercial gel electrodes is 23.91.
I also transferred Zn metal onto other water-soluble substrates, like commercial water-soluble tape and electrospinning porous PVA. Water-soluble tapes from Smartsolve company are purchased and Zn metal layer can be transferred onto the tape. The adhesion of the tape makes it a good contact between human skin and the tape. This is also a low cost and easy-fabrication method for ECG sensor. Figure 3.10 is the ECG signal from water soluble tape/Zn electrode.

Figure 3.10 is a series of ECG signal collected from water soluble tape/Zn electrode. The SNR is 18.89 and we can observe that there is almost no drifting of the signal. The reason is that the adhesive tape makes the electrode quite stable to the skin.
Electrospinning is a method that produces nanometer-scale fibers by applying high voltage and drawing charged fibers from polymer solutions. Porous PVA fibers can be fabricated by electrospinning. Figure 3.11 illustrates the schematic process of electrospinning for PVA electrospun fibers.

Figure 3.10 ECG signal from water soluble tape/Zn electrode.

Figure 3.11 Schematic fabrication process for electrospinning.
Electrospun PVA-Zn electrodes are air-permeable. The air-permeable electrodes can reduce the risk of inflammation and helps the comfortability for the long term use [44]. Figure 3.12 are the simultaneous ECG signals from electrospun PVA/Zn electrodes and commercial gel electrodes. The SNR of electrospun PVA/Zn electrodes is 19.43 and the SNR of commercial gel electrodes is 18.41. They are very closed value indicating same-level sensing performance.

(A)
Figure 3.12 (A) ECG signal from electrospun PVA/Zn nanomesh electrodes (blue line) and (B) ECG signal from commercial gel electrodes (red line).

In order to check the air permeability of electrospun PVA fibers, the water-vapor transmission rate is estimated by putting the electrospun PVA nanomesh onto a tube with distilled water. The weight loss rate of water inside tube is 1.15 mg/cm²/hour for electrospinning fibers and 1.75 mg/cm²/hour for open bottle without lid at 20 °C in figure 3.13. These values are lower than previous reported value [45]: The weight loss rate of water for elastomer sponges is 23 mg/cm²/hour and 42 mg/cm²/hour for an open bottle at 35 °C. The main reason for the difference is the change of temperature.
Figure 3.13 weight loss of water evaporation with time.

3.5 Electromyography (EMG) signals

The EMG sensor can record the electrical potential generated by muscle cells and therefore the sensor can detect the activity of muscle contractions. Direct EMG detection need the electrodes to insert into muscle tissue while surface EMG detection only need to put EMG sensor onto skin surface above muscle. Surface EMG need at least two electrodes to detect the signal because EMG records potential difference between two electrodes. Surface EMG can only measure superficial muscles and it is difficult to pin down the signal to a single muscle. However, the advantage is that it is a noninvasive manner and it is convenient for operation. Real-time muscle activity signals can be utilized for the control of prosthetic limbs and gesture control. The EMG sensor can be useful
for detection of neuromuscular diseases. The frequency of EMG signal is normally between 15-400 Hz [46]. The intensity of muscle contraction will affect the amplitude of EMG signal, normally from micro- to milli-Volts.

Figure 3.14 experimental setting for bicipital muscle EMG signal.

Here we acquire the EMG signal from the contraction of bicipital muscle of arm (figure 3.14). In figure 3.15, we can find that the signal of PVA-Zn electrode is comparable with commercial gel electrode. The SNR of PVA/Zn electrode is 4.94 and the SNR of commercial gel electrode is 8.01. The commercial gel electrodes have less noise of signal in this case.
Figure 3.15 (A) EMG signal from PVA/Zn electrode (blue line) and (B) EMG signal from commercial gel electrode (red line).
3.6 Zn/PVA membrane as temperature sensor

There are several mechanisms of temperature sensors: thermocouples, resistance temperature detector (RTD), resistance temperature detector (RTD) and semiconductor temperature sensor.

Thermocouples consist of two joined different metals. The temperature difference of two dissimilar conductors results in a voltage difference between two metal substances. This is called the Seebeck effect. By measuring the voltage difference, we can measure the temperature change. Nickel Chromium/Nickel Aluminium is one set of thermocouples. Other common thermocouples include Nickel Chromium/Constantan, Iron/Constantan, Copper/Constantan and Platinum Rhodium [47]. Most of the thermocouples can sense temperature from less than -40 °C to more than 1000 °C.

The mechanism of resistance temperature sensor is simple: the electric resistance changes with the change of temperature. Platinum is one common metal that is used as resistance temperature sensor because it provides a linear electric resistance change when temperature changes. In Ning Yi’s paper [48], it also shows that the deposition Zn can be a resistance temperature sensor and the relationship between the change of temperature and the change of electric resistance is linear. This type of temperature sensor requires excitation current.

The junction voltage across a p-n combination is a function of temperature. Usually it is built based on integrated circuit and has linear outputs and relatively narrow sensing range (-40 °C--120 °C).

Here the PVA-Zn electrode can be a temperature sensor to measure skin temperature (Figure 3.16). The mechanism is based on the change of electric resistance due to different temperature. Since Zinc is metal, the resistance increases with temperature rise. The reason of choosing resistance temperature sensor is because of its simple structure and ease of fabrication. What is more, it can
be easily assembled with flexible substrate. The serpentine pattern is designed in AutoCAD software and the PI film shadow mask is prepared by laser cutting.

![Patterned Zn/PVA membrane as temperature sensor](image)

Figure 3.16 Patterned Zn/PVA membrane as temperature sensor

In order to calibrate the temperature sensor, the temperature sensor was connected to a digital multimeter (DMM) (34401A Multimeter) at a probe station (Formfactor 10000). The stage of the probe station can provide temperature change ranging from -60 to 300 °C. The relationship between the temperature and resistance can be described by linear equation $R = R_{ref}[1 + \alpha(T - T_{ref})]$. Here $R_{ref}$ and $T_{ref}$ are reference resistance and reference temperature respectively. $\alpha$ is called the temperature coefficient of resistance (TCR). TCR in the curve is calculated as $0.774e^{-3}$ when $T_{ref}$ is 0 °C and the reference resistance $R_{ref}$ is 627.14Ω. As is shown in figure 3.17, the relationship between temperature change and resistance change is linear.
3.7 Dissolving properties

The PVA-Zn sensor dissolves into hot water within several minutes. The PVA film doesn’t dissolve into cold water after photonic sintering process. The reason is because that the PVA film begin the dehydration and oxidation at around 200 °C and form conjugate bonds and carbonyl groups [49]. The PVA-Zn sensor can dissolve into water with temperature above 70 °C. Figure 3.18 is the dissolving process of PVA/Zn membrane in hot water (90 °C).
Figure 3.18 demonstration of dissolving PVA/Zn electrode in 90 °C water.
Chapter 4 Finite element analysis of graphene-nanomesh (GNM)/single wall carbon-nanotube (SWNT) hybrid membrane

Graphene has attracted attention these years for its excellent mechanical properties, for example, it has 25% fracture strain and Young’s modulus as high as 1TPa. It also has good optical transmittance, high electric carrier mobility and piezoresistive sensitivity. With all these properties, graphene is a good candidate for flexible electronics.

Carbon nanotubes (CNTs) are also a potential material for flexible electronics because it also has good conductivity, flexibility and high intrinsic carrier mobility. Carbon nanotubes can be channel material in filed effect transistors (FETs) and it can also be conductive transparent electrodes. Carbon nanotubes can be used for COMS inverters in flexible circuit. The single wall nanotubes-based transistors can be used for flexible radio frequency device. SWNT-based flexible FETs can also be chemical and biological sensors.

Hybrid film of graphene/carbon nanotube have better performance than single layer of graphene or carbon nanotube in some fields. Hybrid film are designed for electric microheater [50] and high-efficiency electron emission sources [51]. Based on previous study about ion and molecular nanofiltration [52], the combination of these two materials will increase mechanical properties such as Young’s modulus and bending stiffness. Here a finite element analysis of graphene-nanomesh/carbon-nanotube hybrid membrane will calculate the combined Young’s modulus and show the improvement of mechanical properties. The study includes three parts: 1. finite element analysis of the SWNT network; 2. analysis of the mechanical performance of GNM structure and 3. Finite element analysis of the GNM/SWNT membrane.
4.1 Finite element analysis of the SWNT network

The SWNT membrane consists of randomly arranged SWNT bundles and the porous structure make the membrane stretchable. Stretchable lattice structure can be used for the modeling of porous, fibrous materials. Stretchable lattice structures include honeycomb structure, triangle structure and wavy triangle/honeycomb structure. Here we choose classic honeycomb structure because the SWNT showed isotropic property in experiment. The main purpose of this simulation is to obtain the effect of heterogeneous two-layer structure under stretching and bending. The scale is 1000 compared to the real size in order to model in continuum region. In the simulation, the thickness t and length of honeycomb lattice l is 50 um and 160um respectively. The relationship between effective Young’s modulus of honeycomb structure and the Young’s modulus of material is as follows:

\[ E_{\text{structure}} = 2.3E_{\text{material}} \left( \frac{w}{l} \right)^3 \]

Here w and l are the width and length of the lattice cell element separately. Linear model is accurate enough because of small deformation (5% stretching). For the material property, the Young’s modulus \( E_{\text{material}} \) is 1TPa and Poisson’s ratio is 0.19. In order to fit the experimental effective Young’s modulus \( E_{\text{structure}} \) as 2.6GPa, the width of honeycomb lattice w in simulation is chosen as 17.36 um.
4.2 Analysis of the mechanical performance of GNM structure

The graphene layer is perforated with triangular holes and the effective Young’s modulus can be represented in the form of the volume porosity \( f \) [53]:

\[
E_{\text{perforated}} = (1 - 2.988f + 5.624f^2 - 8.306f^3 + 5.455f^4)E_{\text{material}}
\]

The volume porosity \( f \) is 7.9\% from experimental data [52] and we can get the effective Young’s modulus as 794 GPa. For the hybrid GNM/CWNT membrane, we can use a smooth layer of graphene with 794 GPa effective Young’s modulus as is shown in figure 4.2.
4.3 Finite element analysis of the GNM/SWNT membrane

A uniform graphene layer with 794 GPa Young’s modulus, 0.16 Poisson’s ratio and 0.34um thickness are used to replace the perforated graphene layer. By doing this, we can make the calculation easier. The GNM layer and the SWNT layer are bonded together in the simulation. Another extreme case is that there is no bond between the GNM layer and the SWNT layer. The load condition is 5% strain uniaxial stretching. We can observe the max principal strain occurred at the place where GNM and SWNT are bonded together. The effective Young’s modulus of heterogenous GNM/SWNT double layer is 12.8GPa under perfect bonding condition. While the value become 7.95GPa if two layers are separate without bonding. From these two values, the structure of Porous SWNT bundles indeed change the stress/strain distribution at the interface of SWNT/GNM. The real Young’s modulus of GNM/SWNT membrane should be in the range of 7.95GPa to 12.8GPa since π-π interaction and van der Waals interaction should be weaker than entire bond and stronger than no bond conditions. The increased Young’s modulus of
GNM/SWNT comparing with the GNM membrane only indicates that better mechanical performance are achieved by this kind of heterogeneous assembly. The tensile stiffness of GNM/SWNT membrane is calculated as $6.45 \times 10^5$ N m$^{-1}$ and the tensile stiffness of GNM membrane is $2.71 \times 10^5$ N m$^{-1}$. For the application about ion and molecular nanofiltration, higher mechanical stiffness means the better performance of sustaining liquid pressure and therefore, there would be less risk of crack formation for the membrane [52].

Figure 4.3 Mises stress contour of GNM/SWNT membrane after 5% stretching
4.4 Bending stiffness of GNM and GNM/SWNT membrane

The bending stiffness of GNM can be calculated as

\[ \bar{E}I_{\text{GNM}} = \bar{E}_{\text{GNM}} h_{\text{GNM}}^3 / 12 \]

\( \bar{E}_{\text{GNM}} = E_{\text{GNM}}/(1 - \nu_{\text{GNM}}^2) \) is the plane-strain Young's modulus and the poisson’s ratio is 0.16. The thickness of the GNM membrane is \( h_{\text{GNM}} = 0.34 \) µm.

The bending stiffness of the bi-layer GNM/SWNT layer (\( \bar{E}I_{\text{GNM/SWNT}} \)) can be calculated as [54]

\[ \bar{E}I_{\text{GNM/SWNT}} = \sum_{i=1}^{N} \bar{E}_i h_i [(b - \sum_{j=1}^{i} h_j)^2 + (b + \sum_{j=1}^{i} h_j) + 1/3 * h_i^2] \]
Where \( b = \sum_{i=1}^{N} E_i h_i (\sum_{j=1}^{i} h_j - 0.5 * h_i) / \sum_{i=1}^{N} E_i h_i \) is the distance between the neutral mechanical plane to the bottom surface.

\( E_1 = \frac{E_{\text{GNM}}}{(1 - \nu_{\text{GNM}}^2)} \) = 814 GPa and \( h_1 = h_{\text{GNM}} = 0.34 \mu\text{m} \) are the plane-strain Young’s modulus and thickness of the GNM layer. \( E_2 = \frac{E_{\text{SWNT}}}{(1 - \nu_{\text{SWNT}}^2)} \) = 2.7 GPa and \( h_2 = h_{\text{SWNT}} = 50 \mu\text{m} \) are the plane-strain Young’s modulus and thickness of the SWNT layer.

The bending stiffness is \( 8.56 \times 10^{-5} \text{N}\cdot\text{m} \) for the GNM/SWNT membrane. It is much higher than that of GNM membrane. Flexible and stretchable SWNT network mechanically reinforces the GNM membrane and enhances the deformation-resistance of GNM membrane.
Chapter 5 Conclusion

In this thesis, a heterogeneous flexible and transient PVA/Zn electronics are fabricated by photonic sintering. Three applications, ECG sensor, EMG sensor and temperature sensor are applied by this PVA/Zn functional assembly. Some parameters, like the thickness of PVA membrane, size of Zn electrodes need further studies. The encapsulation layer can be added later to prevent oxidation of metal layer after photonic sintering. Another simulation about heterogenous assembly, GNM/SWNT membrane is calculated under uniaxial stretching condition. This simulation focus on the equivalent modeling of porous multilayer structure at nanoscale. The Young’s modulus of bilayer structure should between the range from 7.95 GPa to 12.08 GPa which is consistent with experimental data [52].
References


