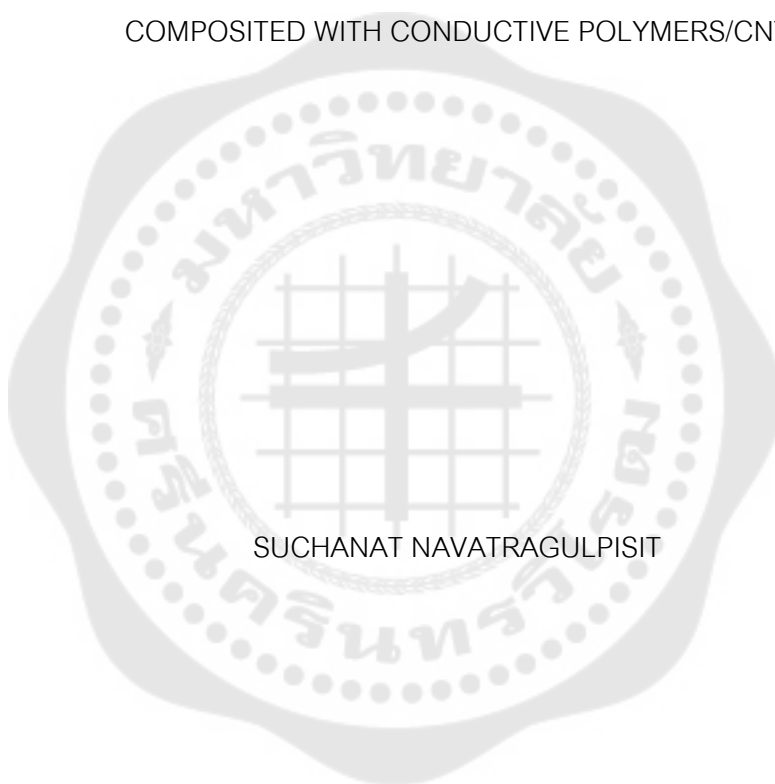




HYBRID TRIBOELECTRIC-THERMOELECTRIC NANOGENERATOR BASED ON FABRIC  
COMPOSITED WITH CONDUCTIVE POLYMERS/CNT



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อุปกรณ์ผลิตพลังงานไฟฟ้าขนาดเล็กไฮบริดจัสโทรโบอิเล็กทรอนิกส์-เทอร์โมอิเล็กทรอนิกส์บนพื้นฐานของผ้า  
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HYBRID TRIBOELECTRIC-THERMOELECTRIC NANOGENERATOR BASED ON FABRIC  
COMPOSITED WITH CONDUCTIVE POLYMERS/CNT



A Thesis Submitted in Partial Fulfillment of the Requirements  
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THE THESIS TITLED  
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| Title          | HYBRID TRIBOELECTRIC-THERMOELECTRIC NANOGENERATOR BASED ON<br>FABRIC COMPOSITED WITH CONDUCTIVE POLYMERS/CNT |
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Nowadays, the electronic textiles (e-textiles), a combination of textiles and electronic components have gained much attention along with the attention of a textile-triboelectric nanogenerator (T-TENG) to be utilized as energy system in e-textiles. However, the continuous contact and friction mechanism of T-TENG leads to generating some waste heat which is the driving force of temporary charges formation. In addition, this pain point producing an unstable output voltage with low output current that limits their performance. Therefore, the aim of this work is to improve T-TENG efficiency by combining it with thermoelectric nanogenerator (TEG) as a hybrid TENG-TEG system. This work focused on the modification of cellulose based fabric (Rayon and cotton fabric) by adding conductive polymers and conductive polymers/carbon nanotube (CNT) as thermoelectric materials. Both conductive polymers of poly(3-hexylthiophene) (P3HT) and polyaniline (PANI) are studied. The facile strategy of ultrasonicated dip-coating is used. Therefore, the hybrid TENG-TEG device in this work is fabricated by using cellulose-based fabric/conductive polymers in various systems (Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT) as main friction materials to enhance the output performance. The composite fabrics characterization and conductive polymers distribution are examined. Also, the thermoelectric properties, electrical properties and output efficiency are investigated. As shown in the results, it was found that the greater thermoelectric and electrical performance of hybrid TENG-TEG in various system related to the addition of conductive polymers. Accordingly, the Rayon/P3HT 150 mg showed the electrical output of  $\sim 63$  V and  $\sim 45$   $\mu$ A for open-circuit voltage ( $V_{oc}$ ) and short-circuit current ( $I_{sc}$ ), two times higher than using pristine Rayon. Meanwhile, the Rayon/PANI and cotton/PANI at optimum condition presented the larger electrical properties and output efficiency than pristine cellulose-based fabrics. However, it demonstrates the fluctuation results between electrical properties and electrical output. So, the cotton/PANI/CNT three phases composite are studied. It was found that the cotton/PANI/CNT 1.50 g obviously showed the best performance with the maximum Seebeck coefficient of 98.5 mV/K and the  $V_{oc}$  and  $I_{sc}$  of  $\sim 40$  V and  $\sim 77$  mA. The  $P_{max}$  reaches  $\sim 263$   $\mu$ W, 5.3 times higher than pristine cotton. Furthermore, a hybrid TENG-TEG contains capability to light up 100 LEDs in series circuit connection and can be applied as power supply for drive various of small-electronic devices. The high performance of hybrid device in this work leads to have a chance to advance into E-textiles system for commercial use in the future.

Keyword : Cellulose-based fabric, Polyaniline, Poly(3-hexylthiophene), Carbon nanotube, Hybrid triboelectric-thermoelectric nanogenerator

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## CHAPTER 1

### INTRODUCTION

#### Background and significance of the research

In this era, electronic textiles (e-textiles), a combination of textiles and electronic components, have gained much attention and tend to be developed for the new generation with more comfortable use (1). The global trend of e-textiles in smart clothing market shows an expectation of annual growth rate (CAGR) for 32.3% from 2021 to 2028 (2). Nevertheless, embedded electronic components basically require energy power from batteries for operation that is limited for long-term use (3,4). To solve the issue, the harvesting of ambient energy, energy sources from an environment surrounding, then substitute for new generation of power supply device. Among the ambient energy, *i.e.*, light, wind, water thermal and so on, the mechanical energy is abundant and contains the capability of all-time harvesting (5). Nowadays, mechanical energy harvesters (MEH) including piezoelectric nanogenerator (PENG) and triboelectric nanogenerator (TENG) play a crucial role in high efficiency and sustainability (6). For comparison, TENG is candidate in terms of the highest energy conversion efficiency and broadly being powered supply device for several applications (7).

The TENG device was discovered by Prof. Zhong Lin Wang and *et.al*, in 2012. The harvesting mechanism is based on fundamental effects of triboelectrification and electrostatic induction that easily creates by friction of two different types of materials (8). In general, the materials with highly different electron-captured abilities including tribo-positive and tribo-negative material consist in TENG's structure to produce an effective output. A variety choice of materials for TENG provides possibility to integrate with e-textiles system. Many fabrics, such as silk (9), cellulose-based fabric, nylon (10), polyester (11) are commonly considered owing to the flexibility, breathability and compatibility with the human body. Cellulose-based fabrics are getting attention in this work due to their high abundant and potential chemical structure. Containing a lot of the hydroxyl group (-OH) shows high potential for electron donation. Among the variety of

cellulose-based fabrics, cotton is famous. Fabricating TENG by using cotton show favoring with variety of contact layer. In 2016, the cotton based TENG was fabricated by contacting with nylon fabric. The open circuit output voltage ( $V_{oc}$ ) and short circuit output current ( $I_{sc}$ ) of 1.5 V and 0.3  $\mu$ A was obtained (12). The cotton based TENG in different pattern of plain and 2/1 twill weave generated the output performance of 1.59 V and 12.49 V (13). Also, in the following year, cotton TENG provided 39.23 V and 0.20  $\mu$ A (14) after friction with silk. However, it can be seen that the low output efficiency needs to be developed. There are various methods to improve TENG efficiency. In 2019, the cotton based TENG with modified porous Teflon could generate about 660 V and 12.5  $\mu$ A (15). The conductive cotton electrode was merged with cotton based TENG to reached the output efficiency of 557 V and 26  $\mu$ A (16). Also, the cotton based TENG was designed in different structure, the 3D-angle interlock could generate 100 V and 12.5  $\mu$ A (17) while in free-standing mode reached about 789 V with 8.9  $\mu$ A (18). Even though cotton-based fabrics can be modified as contact materials for TENG, the obtained  $I_{sc}$  is still low because of the temporary charge generation. According to the triboelectric mechanism, the triboelectric charges can be stayed on the material surface for a while with having possibility to loss (19). Also, repeating in contact-separation of materials causes the waste heat as another driving force to let the charges lose. Up to now, there are several methods to improve the TENG efficiency such as surface modification (20), chemical functionalization (21), structure design (22) and hybrid system modification *etc.* (23). In particular, the combination of energy harvesting mechanism to harvest various kinds of energy sources within one device, known as the hybrid system, are in demand such as hybrid triboelectric-thermoelectric nanogenerator (hybrid TENG-TEG) (24), hybrid triboelectric-photovoltaic nanogenerator (hybrid TENG-PV) (25), hybrid triboelectric-piezoelectric (hybrid TENG-PENG) (26) and hybrid triboelectric-electromagnetic nanogenerator (hybrid TENG-EMG) (27). Among them, the hybrid TENG-TEG get attention due to the ability of the TEG materials to convert thermal energy into electricity (24, 25). When a temperature gradient occurs, the charge carriers come across to the other side of TEG based on the Seebeck effect and generate the

electrical output (28). Therefore, the waste heat can be solved and the high  $I_{sc}$  generation of TENG-TEG can be produced by simultaneous harvesting of mechanical energy and waste heat energy gaining from triboelectric mechanism (19). The hybridization of TENG-TEG, confirm the greater charge efficiency by 87% by comparing to ordinary TENG (29). However, the fabrication of hybrid TENG-TEG usually focused on the structural design, i.e., disk shape of shape-memory alloy and flexible TEG (30), rotary shape of nylon and Teflon with bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) (29), and tiles shape of polydimethylsiloxane (PDMS) and  $\text{Bi}_2\text{Te}_3$  (31). Meanwhile fabric modification is still rare.

By taking TEG into account, the fabrication of TEG for merging with e-textile system prefer the wearability and flexibility. However, the most highly efficient TEG materials are ceramics which is large Seebeck coefficient but still lack of flexibility. Fabricating flexible TEG for e-textiles is therefore normally done by embedding the small pieces TEG into flexible fabric template. K. Jin and co-workers fabricated the TEG by embedding  $\text{Bi}_2\text{Te}_3$  and antimony telluride ( $\text{Sb}_2\text{Te}_3$ ) ceramics on glass-fabric generating 90 mV and  $3.8 \text{ mW/cm}^2$  at a temperature gradient of 50 K (32). K. Min-Ki and *et.al* presented the laced  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  and  $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$  TEG in clothes to get the 14.2 mV and 15.8  $\mu\text{A}$  of output at 15 K of temperature gradient (33). In the same way, Y. Yang and co-workers reported the harvesting a waste heat from human body with the embedded  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  TEG device in clothes to provide 117 mV and 5.4 mA (34). Even though the TEG fascinates to overcome the limitation of  $I_{sc}$ . Nevertheless, the solid conventional TEG materials embedded on flexible substrate limit their flexibility to only one direction. All flexible and stretchable materials in textiles-based hybrid TENG-TEG are challenges. The conductive polymers become candidates for new TEG materials, owing to their excellent thermoelectric properties with flexibility, lightweight, and available use at room temperature (35). Y. Zhang and *et.al.* studied various kinds of conductive polymers that qualified thermoelectric properties including polyacetylene (PAC), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), polythiophene (PT), poly(3-hexylthiophene) (P3HT) and Nafion (36, 37). Among them, PANI and P3HT are outstanding because of the wide range of electrical conductivity nearby room

temperature (38, 39) that suitable for collecting heat from human body by incorporating in e-textiles. Compositing those conductive polymers with carbon nanotube (CNT) even push forward the electrical conductivity by reaching 1,440 S/cm for PANI/CNT (39) and 579 S/cm in P3HT/CNT (40).

This work focused on the modification of cellulose based fabric with adding conductive polymer for hybrid TENG-TEG fabrication. The facile strategy of ultrasonicated dip-coating is used. Various amounts of conductive polymer including PANI and P3HT and conductive polymer/CNT composites on fabrics are studied relative to the characteristics and electrical output signal. The surface morphology of fabrics and fabric composites are examined by scanning electron microscopy (SEM) and light optical microscopy (LOM). The distribution of conductive polymer and conductive polymers/CNT inside fabrics is examined by Synchrotron radiation X-ray tomographic microscopy (SR-XTM). Infrared spectroscopy (IR) and Raman spectroscopy (Raman) are used to confirm the functional groups and the fingerprint of the fabrics, conductive polymers/CNT and fabrics/conductive polymers/CNT three phase composites. The electrical properties including impedance, conductivity and resistivity are measured by LCR-meter. The electrical output signal of open circuit output voltage ( $V_{OC}$ ), short circuit output current ( $I_{SC}$ ) and maximum output power ( $P_{max}$ ) of all samples are investigated using oscilloscope and digital multimeter (DMM) with sliding mode operation. Furthermore, the practical applications of the hybrid TENG-TEG for real-time driving portable devices *i.e.*, digital watch and safety flashing light are aimed to be tested.

### Objectives of the study

1. To prepare the conductive polymer/CNT composites.
2. To prepare fabrics/conductive polymers/CNT three phase composites.
3. To study the characteristics of fabrics, conductive polymer/CNT composites and fabrics/conductive polymers/CNT three phase composites.
4. To fabricate the hybrid triboelectric-thermoelectric nanogenerator (hybrid-TENG-TEG).

5. To study the effect of adding conductive polymer/CNT to fabric on the electrical properties and output efficiency of the hybrid triboelectric-thermoelectric nanogenerator (hybrid-TENG-TEG).

#### Scope of the study

1. Prepare the conductive polymers, including Poly(3-hexylthiophene) (P3HT), Polyaniline (PANI) and their composites with CNT.
2. Prepare cellulose-based fabrics/conductive polymers/CNT three phase composites by ultrasonic dip-coating process.
3. Study the characteristics of fabrics, conductive polymer/CNT composites and fabrics/conductive polymers/CNT three phase composites by scanning electron microscopy (SEM), light optical microscopy (LOM), synchrotron radiation X-ray tomographic microscopy (SR-XTM), infrared spectroscopy (IR) and Raman spectroscopy (Raman).
4. Fabricate the hybrid triboelectric-thermoelectric nanogenerator (Hybrid-TENG-TEG) based on fabrics/conductive polymers/CNT composites operating in sliding mode.
5. Study the effect of adding various amount of conductive polymers/CNT to fabric on the electrical properties i.e., impedance, conductivity, and output efficiency, i.e., open circuit output voltage ( $V_{oc}$ ), short circuit output current ( $I_{sc}$ ) and maximum output power ( $P_{max}$ ) of the hybrid triboelectric-thermoelectric nanogenerator (Hybrid-TENG-TEG).

### Conceptual Framework

The conceptual framework of this work is shown in Figure 1.

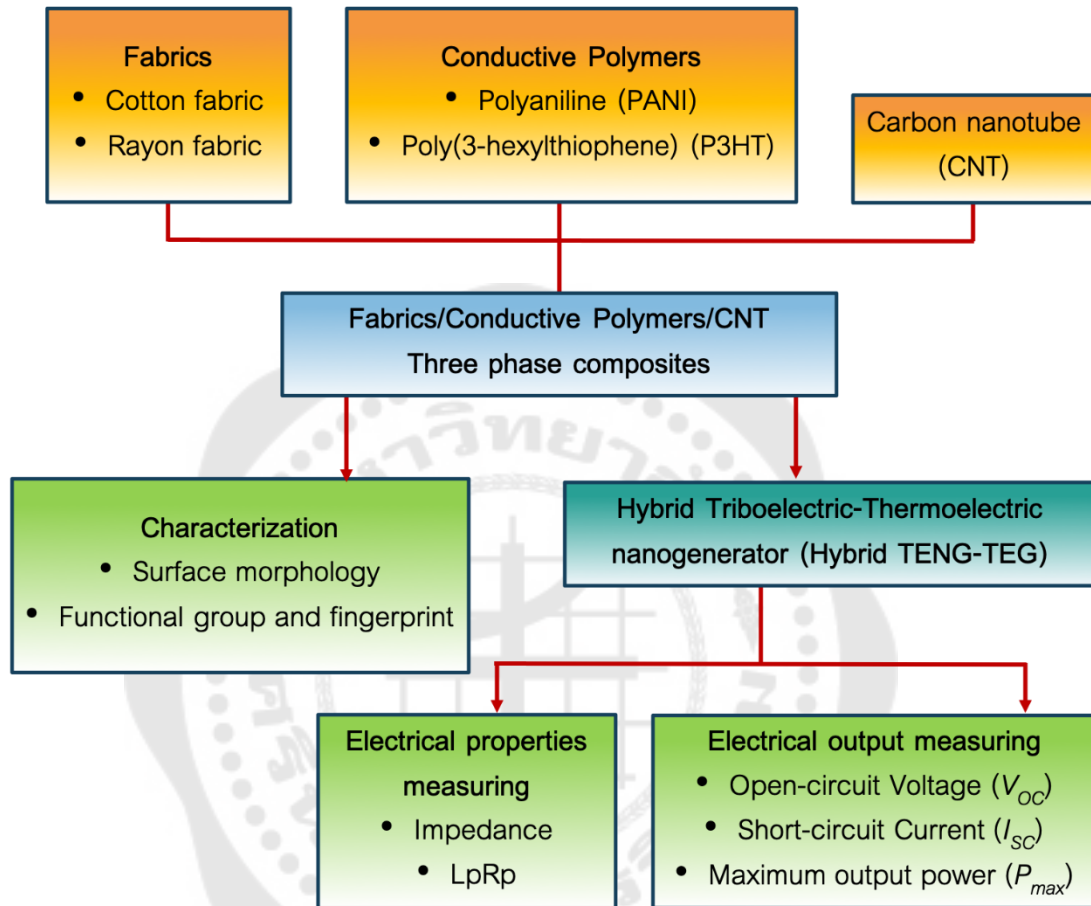


Figure 1 Conceptual Framework

### Expected Outcome

1. Obtain the conductive polymers including Poly(3-hexylthiophene) (P3HT) and Polyaniline (PANI) with their CNT composites.
2. Obtain the cellulose-based fabrics/conductive polymers/CNT three phase composites.
3. Understand the characteristics of fabrics, conductive polymers/CNT composites and fabrics/conductive polymers/CNT three phase composites.

4. Acquire the hybrid triboelectric-thermoelectric nanogenerator (Hybrid-TENG-TEG) based on fabrics/conductive polymers/CNT three phase composites within sliding mode.
5. Understand the effect of adding various amounts of conductive polymers/CNT to fabric on the electrical properties and output efficiency of hybrid triboelectric-thermoelectric nanogenerator (Hybrid-TENG-TEG).



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Electronic textiles (E-textiles)

Electronic textiles or e-textiles are a combination of textiles and electronic components (41). They are a class of wearable device that render human life to be more convenience with an efficient in various fields such as medical, education, fashion, and sport, etc. (42). E-textiles have gained much attention as the forecasting of the global trend of e-textiles & smart clothing market has growth continuously with an expectation of annual growth rate (CAGR) of 32.3% from 2021 to 2028, according to Figure 2 (2). Also, e-textiles are driving the commercial brands to produce a several types of products to satisfy human needs.

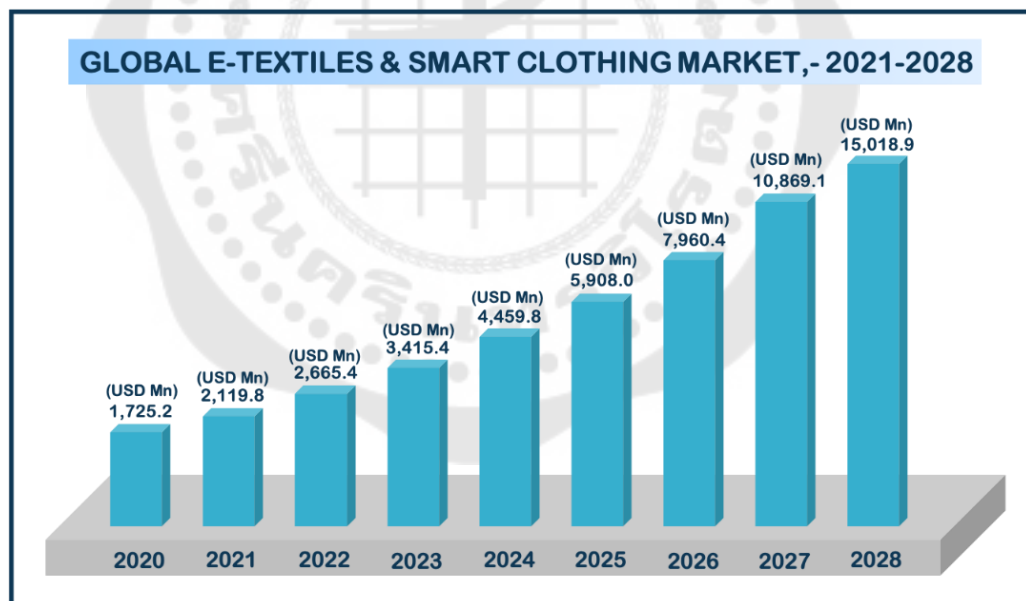


Figure 2 The global trend of e-textile & smart clothing market from 2021 to 2028

Source: <https://www.globenewswire.com/fr/>

The e-textiles are in form of outfits which our body can be wear, including the electronic component such as sensor, actuator, control unit and power supply that embedded into garments for the functional as shown in Figure 3 (3).

#### **2.1.1 Sensor**

A sensor is an electronic device that has the ability to sensing by detecting and responds to the different sources of the input such as heat, light, sound, or motion. The output signal is produced in the form of electrical properties. The common types of sensors that embedded in textile are resistance sensor, temperature sensor and ECG sensor (43).

#### **2.1.2 Actuator**

An actuator is an electronic component that is responsible for converting the energy source such as heat, air, pressure, or electricity to create the motion or control the systems. An actuator has several types that can produce the motion in linear, rotation and bending ways (43).

#### **2.1.3 Control unit**

A control unit is an electronic component that have ability to control and direct operate all of the component in the system such as sensor and actuator to respond properly (43).

#### **2.1.4 Power supply**

The power supply is the electronic device that have ability to delivering a stable power to drive other electronic components by convert the output source of voltage back to the input (43).

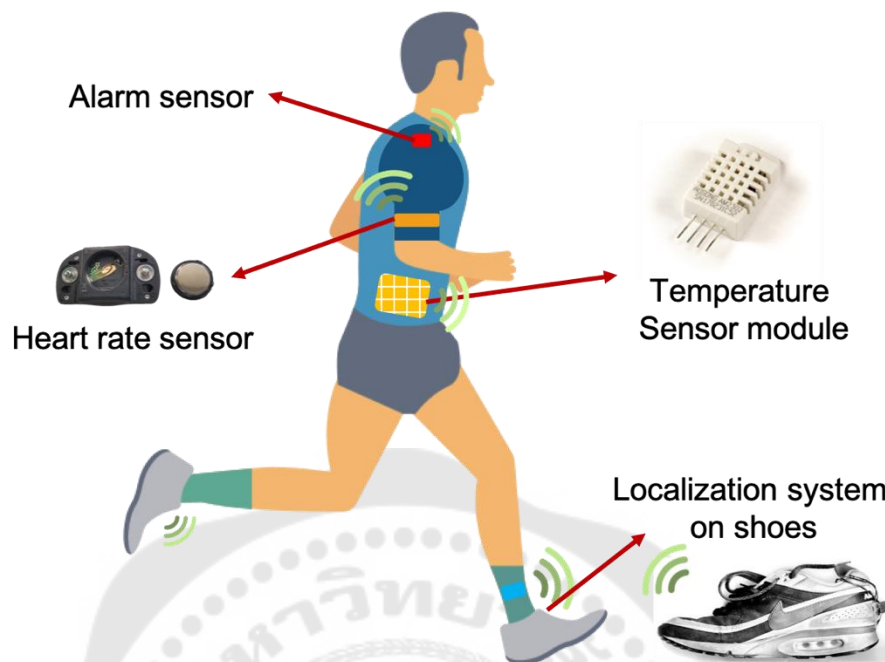


Figure 3 The electronic components in e-textile system

Source: <https://passive-components.eu/embroidered-smart-textiles-electronic-components-in-life-saving-applications/>

The requisite thing is the electronic components that embedded in e-textile system require energy power from the power supply to function. Meanwhile, most of energy power are in form of batteries that still cause some limitation of non-flexible, bulky size, capacity fade and toxicity that need to reduced (3, 4). To solve the issue in a suitable way, the harvesting of ambient energy then substitutes for new generation of power supply device.

## 2.2 The harvesting of ambient energy for e-textile system

Ambient energy harvesting is the process to gain the energy sources from an environment surrounding which is clean, abundant and sustainable to transform into usable electrical energy for various field (5). The common ambient energy sources such

as light, wind and thermal etc. are normally harvested by energy harvester for driving the electrical components in e-textile system as shown in Figure 4.



Figure 4 Ambient energy sources in E-textile system

Source: Muhammad Shahzad Nazir. (2020). Environmental impacts and risk factors of renewable energy paradigm p. 33516-33525.

### 2.2.1 Solar energy harvesting

Solar energy is an abundant energy from sunlight. The radiation of the sun can be converted to the electricity through the energy harvesting devices namely, photovoltaic panels or solar cell (44) with using semiconductor materials. The working principle is explained by the p-n junction that creates different charge carriers and generate the electricity instantly while the sunlight is exposed. For e-textile, the solar panels were immersed to the textile such as bag, clothes or hat as shown in Figure 5 (45) to generate enough power for driven the electrical component in the system.



Figure 5 Solar cell on textiles for driven the portable device

Source: Dong Yang (2019). Polymers p.167.

### 2.2.2 Wind energy harvesting

Wind energy is a clean energy that rapidly grows owing to its sustainable source. This energy has the ability to convert air motion to electricity by wind turbine. The working principle can be explained based on wind motion to change the form of kinetic energy into mechanical energy and produce the electrical energy through wind-energy harvester (46). According to the study by Y. Lai et.al., fabric-based TENG has been fabricated for wind energy harvesting. As shown in Figure 6, this device could harvest wind energy through a flag and coat and transform it to electricity. The TENG act as a self-powered sensor that have enough performance to drive the light-emitting diodes (LEDs) (47).



Figure 6 Wind energy harvesting through a flag and coat

Source: Lai YC (2019). Adv Sci p. 1801883.

### 2.2.3 Thermal energy harvesting

Thermal energy or known as heat energy is an energy that relates to the difference in temperature. The heat can be directly converted into electrical energy through the thermal energy harvester namely, thermoelectric nanogenerator (TEG). The thermal energy harvesting in textile involves the heat source of environment and also from human body to driven the electronic component in the system (48) as shown in Figure 7.



Figure 7 The thermal energy from human body for e-textiles

Source: <https://www.manchester.ac.uk/discover/news/graphene-smart-textiles-developed-for-heat-adaptive-clothing/>

However, harvesting most ambient energy still has some limitations. There are environmental factors of climate and temperature which are uncontrollable due to the sunlight, thermal and wind motion are not all-time exist. Here, mechanical energy harvesting plays a crucial role with high efficiency and capability of all-time harvesting.

### 2.3 Mechanical energy harvesting

Mechanical energy is one kind of renewable energy that is all around human activities. The motion from human or objects such as walking, exercise, sport, texting, structuring, driving etc. as well as sleeping can generate the electricity (49). According to the prominent point of all-time harvested, mechanical energy was chosen instead of other renewable energy due. For convert mechanical energy to an efficient electrical power, the mechanical energy harvester (MEH) is invited. Among several kinds of MEH, piezoelectric nanogenerator (PENG) and triboelectric nanogenerator (TENG) are outstanding owing to their performance (50). In 2018, X. Zhang and et.al. were summarized the power density and energy conversion efficiency for promising technologies of ambient energy harvesting as shown in Figure 8. For comparison



on the surface of materials because of an electron exchange. The materials which are electron donors generate positive while an electron acceptor generates negative charges on its surface. So, the charges balanced and no current to flow at the beginning of attaching process. Until the materials start to separate from each other, the unbalance of triboelectric charges occurred and induced the opposite charges to both electrodes. The difference in the number of charges between the material and electrode, making the charges export to the external load and generate the signal of positive current. When both materials are completely separated, the charges between the surface of materials and electrode are balanced with a stop flowing of the current. While the materials start to contact again, the current is generated and flows in the opposite way in the signal form of negative current resulting in the alternating current (AC) waveform (51).

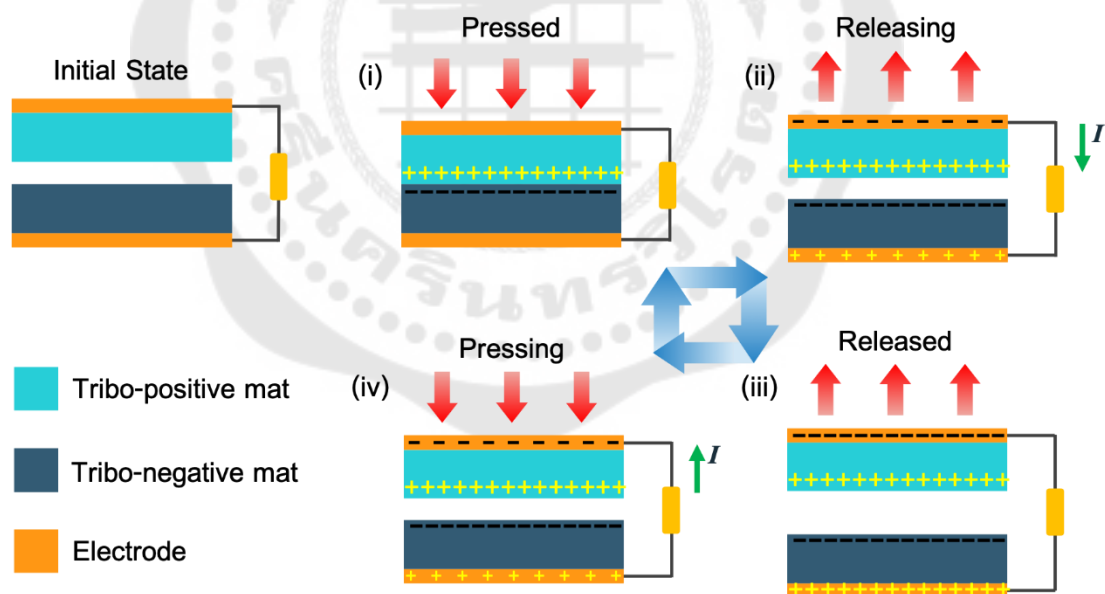


Figure 9 Working mechanism of triboelectric nanogenerator (TENG)

Source: <https://byjus.com/physics/triboelectric-series/>

### 2.4.1 The TENG structures and its working mode

The structures of TENG have four working modes. Including, Contact-Separation mode, Sliding mode, Single-Electrode mode, and Freestanding mode. In each mode relies on different way of friction that present an uncomplicated of the structure as shown in Figure 10.

#### 2.4.1.1 Contact-Separation mode

The contact-separation mode is the most used working mode of TENG owing to their motion in vertical way. The structure of this mode consists of two or more different types of material with an electrode at both ends of structure. In the initial state two materials are separated from each other by having a gap between them. For using this mode as TENG structure, the electricity is generated by the motion of contacting and separating, repeatedly.

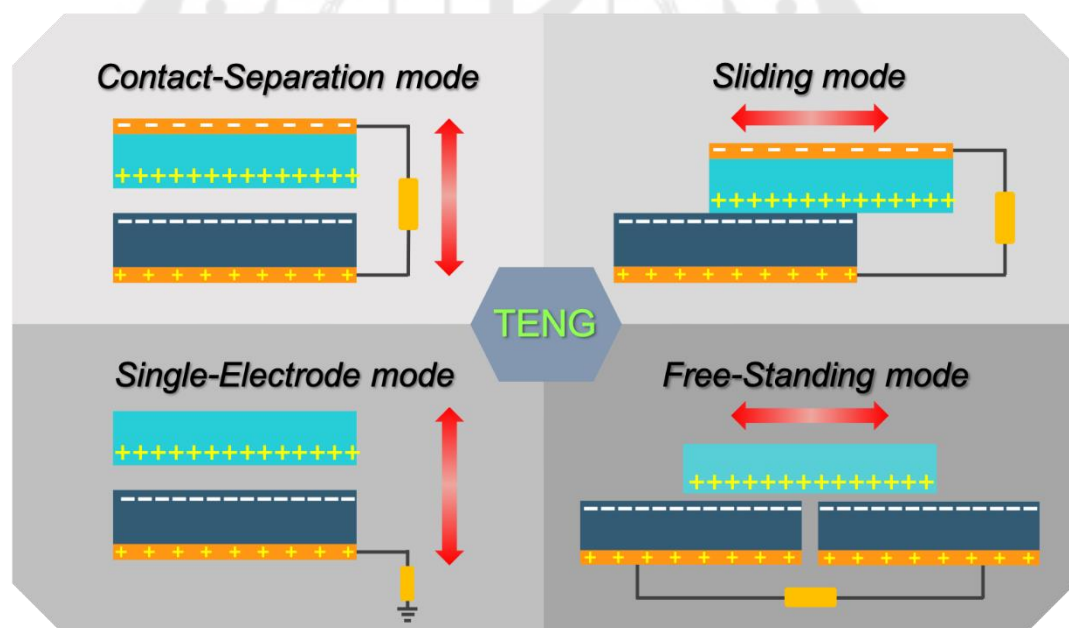


Figure 10 The four structures of triboelectric nanogenerator

Source: <https://byjus.com/physics/triboelectric-series/>

#### **2.4.1.2 Sliding mode**

Sliding mode is the mode that can generate electricity by the motion of rubbing in a parallel way, periodically. The structure of sliding mode consists of two different materials with an electrode at both end of each material. The important point is some parts of the two materials need to touch each other together without separation in all-working time.

#### **2.4.1.3 Single-Electrode mode**

The single-electrode mode is the mode that has only one electrode with one or two materials in the structure. To generate electricity, one of the triboelectric materials can move freely to contact with another materials layer or electrode.

#### **2.4.1.4 Freestanding mode**

The freestanding mode is suitable use with high frequency condition causing to generate the highest electrical output performance compared with other mode. The structure of this mode consists of material that acts as triboelectric layer which can contact in left and right way on the two electrodes that fixed.

In addition to an uncomplicated structure, the variety of choice of materials is another distinctive point that makes TENG get attention. Generally, the structure of TENG consists of two different materials with different electron-captured abilities including tribo-positive material and tribo-negative material. Moreover, choosing the pair of triboelectric materials is one of the most essential factors that relate to the output efficiency of TENG. Thus, the triboelectric series have concluded and act as a key of material selection.

### **2.4.2 Triboelectric series**

The triboelectric series is a summary of a wide variety of materials including various types such as metals, ceramics, polymers, and biomaterials. According to the structure of TENG that consist of two different materials with different electron captured abilities, the tribo-positive materials present the ability of electron donating while the tribo-negative materials present the ability of electron accepting. In the triboelectric series, the tribo-positive materials and tribo-negative materials were

arranged by ranking from the highest positivity to the highest negativity as shown in Figure 11. To fabricate TENG, the pair of triboelectric materials should be in high positivity with high negativity to produce effective output efficiency.

A variety choice of materials for TENG provides possibility to integrate with e-textiles system. Many fabrics such as silk (9), cellulose-based fabric, nylon (10), polyester (11), etc. are also considered owing to the flexibility, breathability, and compatibility with the human body. Cellulose-based fabrics are getting attention in this work due to their potential chemical structure. Containing a lot of the hydroxyl group (-OH) of cellulose-based fabric shows high potential for electron donation. Among the variety of cellulose-based fabrics, cotton is famous.

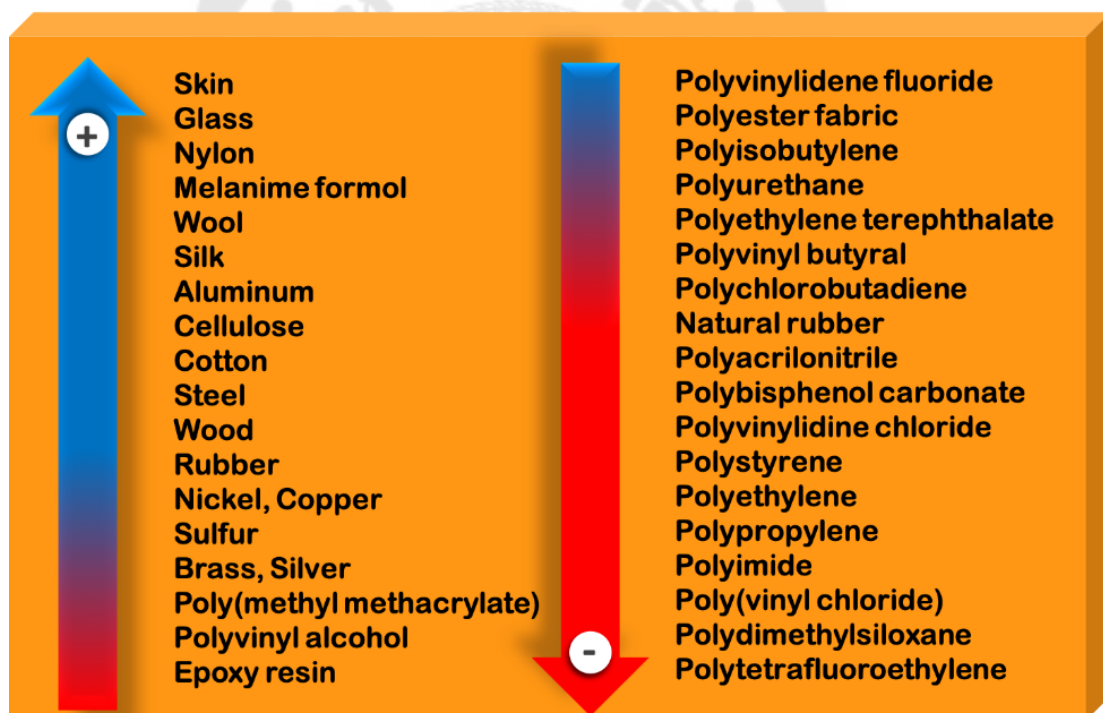


Figure 11 The triboelectric series

Source: <https://byjus.com/physics/triboelectric-series/>

## 2.5 Cotton fabric

Cotton is a fabric that has the component of 96% of cellulose, 1.2% of pectin and 0.6% of wax. The main functional group of cotton is hydroxyl group (-OH) according to the molecular structure as shown in Figure 12. Containing a lot of the hydroxyl group (-OH) shows high potential for electron donation which act as tribo-positive materials.

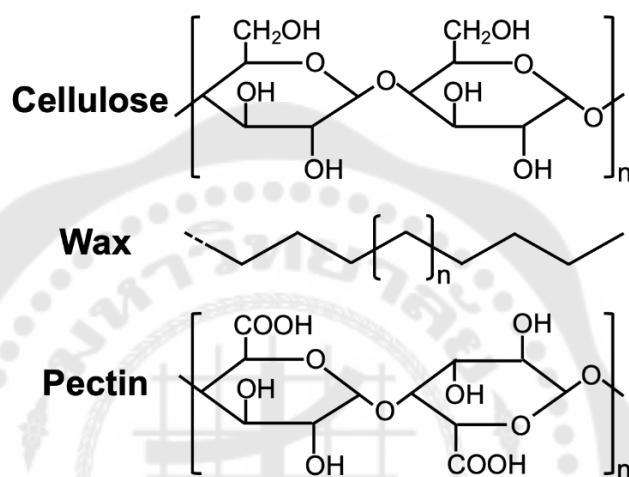


Figure 12 Molecular structure of cotton

Source: <https://www.mdpi.com/2073-4360/11/9/1443>

### 2.5.1 Properties of cotton

The cotton fabric is commonly used in the clothing industry according to Figure 13. The world fiber production graph shows the production of cotton fiber which continuously growth from the past to the future (52) which relates to their properties of comfortability, breathability, absorbency and eco-friendly. Also, the strength of cotton can improve while wetting due to increasing the orderliness of the fiber structure. So, fabricating TENG by using cotton show favoring with variety of contact layer.

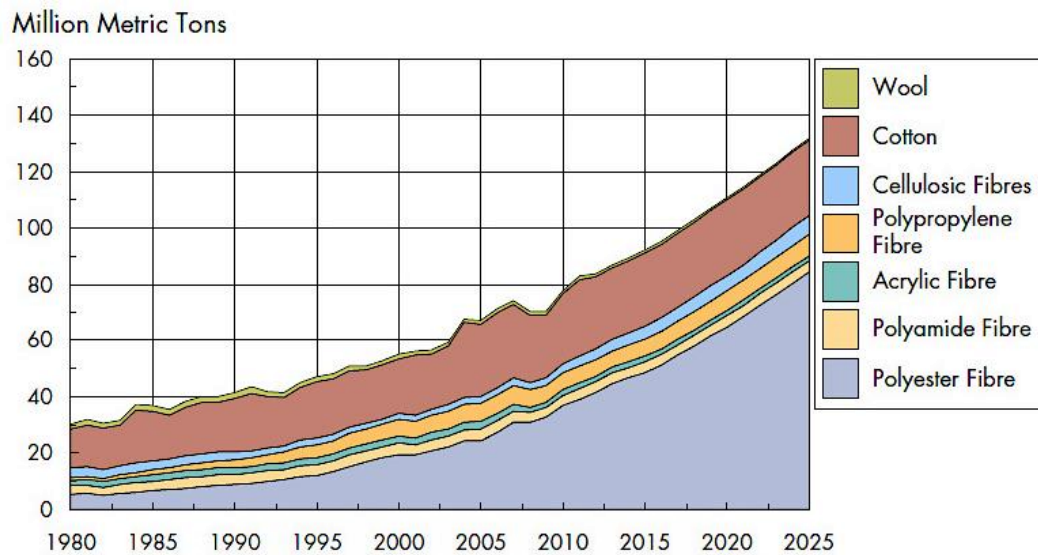


Figure 13 World fiber production

Source: Malgorzata Koszewska. (2018). Autex Research Journal p. 339.

In 2016, L. Zhang and *et.al.* fabricated cotton based TENG with nylon fabric as contact layer. The conductive fabric acted as electrode to obtained all-textile based TENG system. The  $V_{oc}$  and  $I_{sc}$  of 1.5 V and 0.3  $\mu A$  was generated as shown in Figure 14 (12). In 2019, the textile-based TENG was studied by having cotton in different pattern of pain weave (Figure 15a) and 2/1 twill weave (Figure 15b) as tribo-material. The output performance was received with different amounts of 1.59 V and 12.49 V (13). Also, the following year, natural textile- TENG were studied by W. Sangkhun and S. Wanwong. The TENG were fabricated by cotton fabric and silk fabric as tribo-contact material. The output performance was generated about 35.73 V and 0.06  $\mu A$  in cotton-cotton system. While the cotton-pristine silk system generated  $V_{oc}$  of 39.23 V and  $I_{sc}$  of 0.20  $\mu A$ , as shown in figure 16a and b (14). According to the study, it was shown that the low output efficiency of cotton based TENG for both  $V_{oc}$  and  $I_{sc}$  needs to be developed.

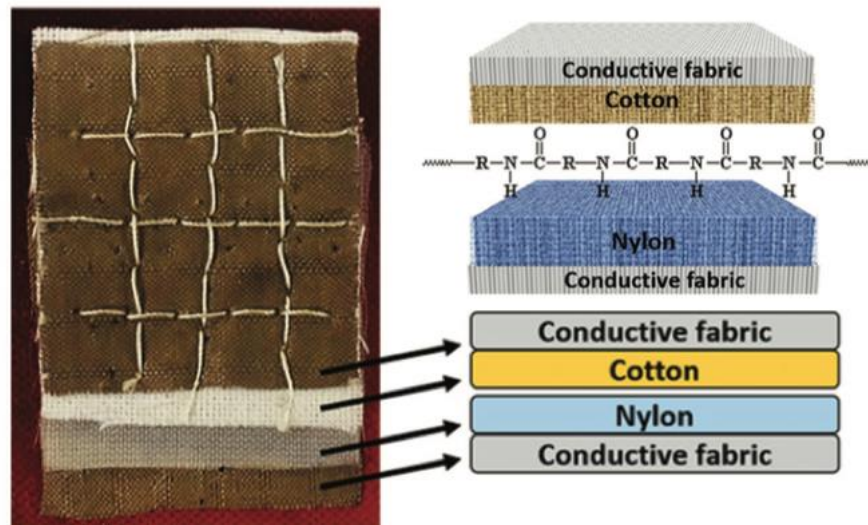


Figure 14 All-textile based TENG by using cotton and nylon as contact layers

Source: Lushuai Zhang. (2016). Advanced Materials Technologies p. 1600147.

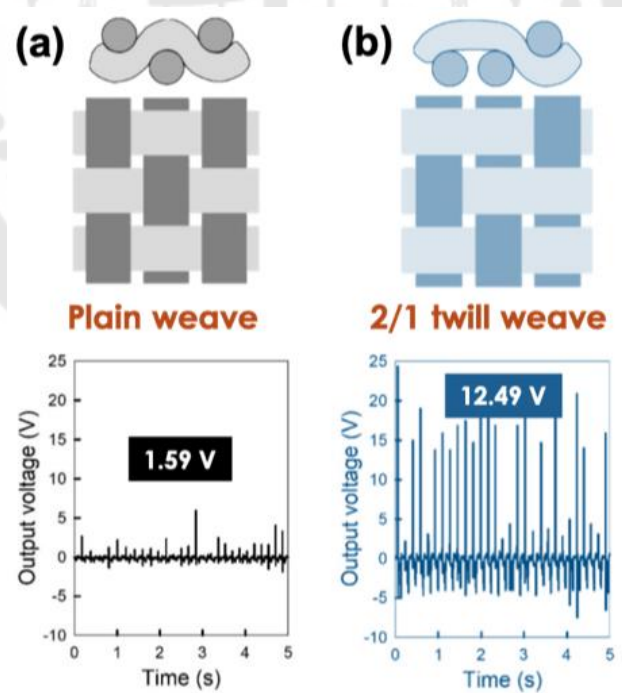


Figure 15 Cotton-based TENG in different pattern of (a) pain weave and (b) 2/1 twill weave

Source: Jaebum Jeong. (2019). Polymers p. 1443.

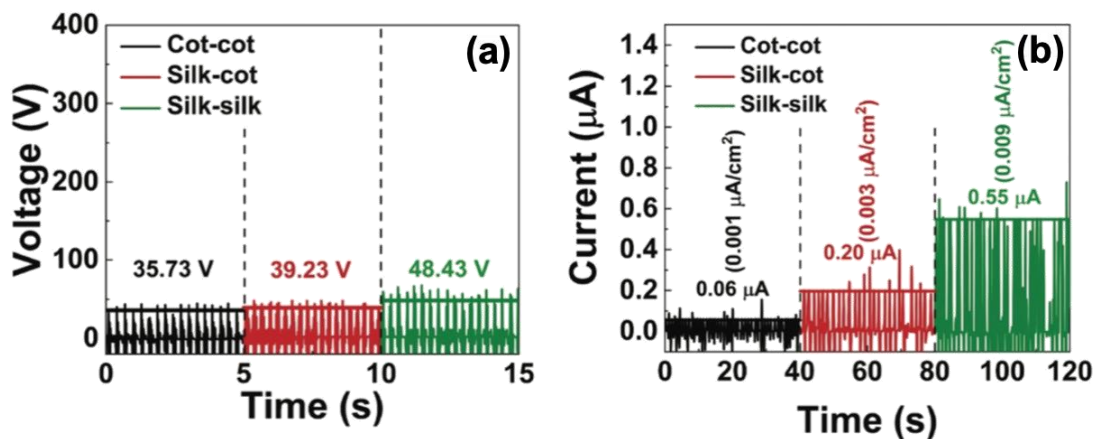


Figure 16 The efficiency of (a) output voltage and (b) output current of natural textile based TENG

Source: Sangkhun W. (2021). *Nanoscale* p. 2420-8.

There are various methods to modify TENG efficiency. In 2019, Y. Tang and *et.al.* have fabricated textiles-based TENG by using cotton and Teflon as tribo-positive materials and tribo-negative materials. The cotton was prepared from clothes while the Teflon was prepared in form of porous structure then fabricated to be self-powered personal electronics by attaching the TENG device on the clothes. The attached device is shown in Figure 17a. According to Figure 17b, the electrical output performance was measured by swing arm motion to operate the electronic watch, running light and LEDs guiding sign, they show that the maximum output voltage  $V_{oc}$  reach to 660 V while  $I_{sc}$  could generate 12.5  $\mu\text{A}$  (15). The coming year, Z. Zhang and *et.al.* designed wearable TENG (W-TENG) by using cotton and Teflon film as triboelectric layers, as shown in Figure 18. The electrode was prepared by cotton coated with conductive ink. The W-TENG was designed especially for the human body. The TENG output performance of 557 V and 26  $\mu\text{A}$  were generated with maximum output power density of 0.66  $\text{mW}/\text{cm}^2$  (16). Also, the cotton based TENG was designed in different structures. The 3D-angle interlock of cotton composite yarn was fabricated by coating with silicone. The output efficiency could generate about 100 V and 12.5  $\mu\text{A}$  as shown in Figure 19 (17). While in Figure 20, wheel-shaped of free-standing mode in cotton based TENG was designed with

fluorinated ethylene propylene film (FEP). The  $V_{oc}$  and  $I_{sc}$  of 789 V and 8.9  $\mu A$  (18) could be reached.

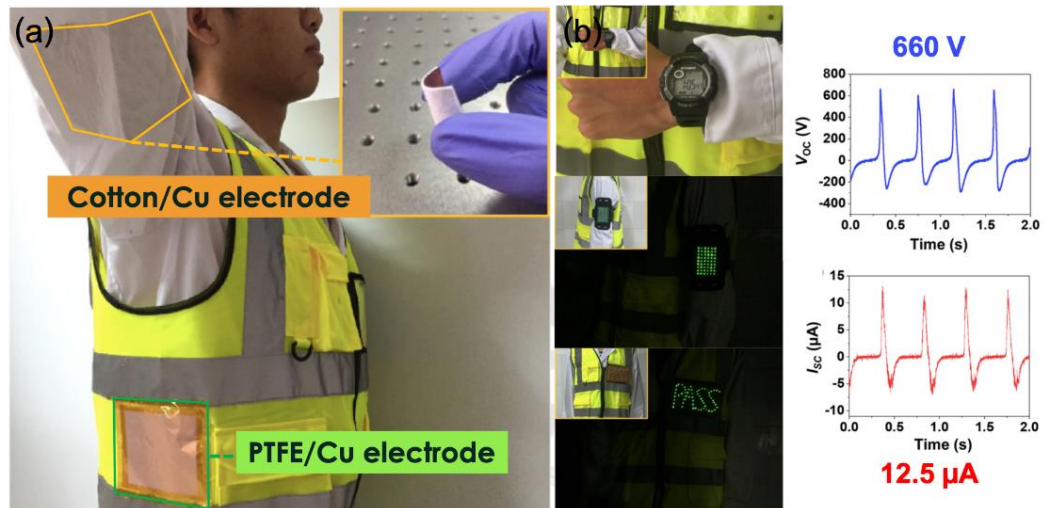


Figure 17 Schematic illustration of (a) self-powered personal electronics and (b) the electrical measurement of textiles based TENG

Source: Tang Y. (2020). J Mater Sci p. 2462-70

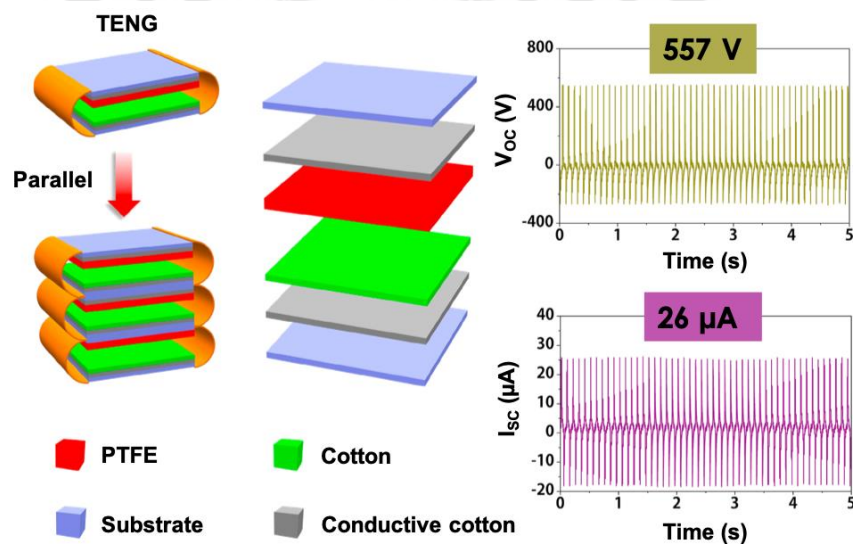


Figure 18 The overview of wearable cotton-based TENG device

Source: Zhang Z. (2021). Current Applied Physics p. 1-5.

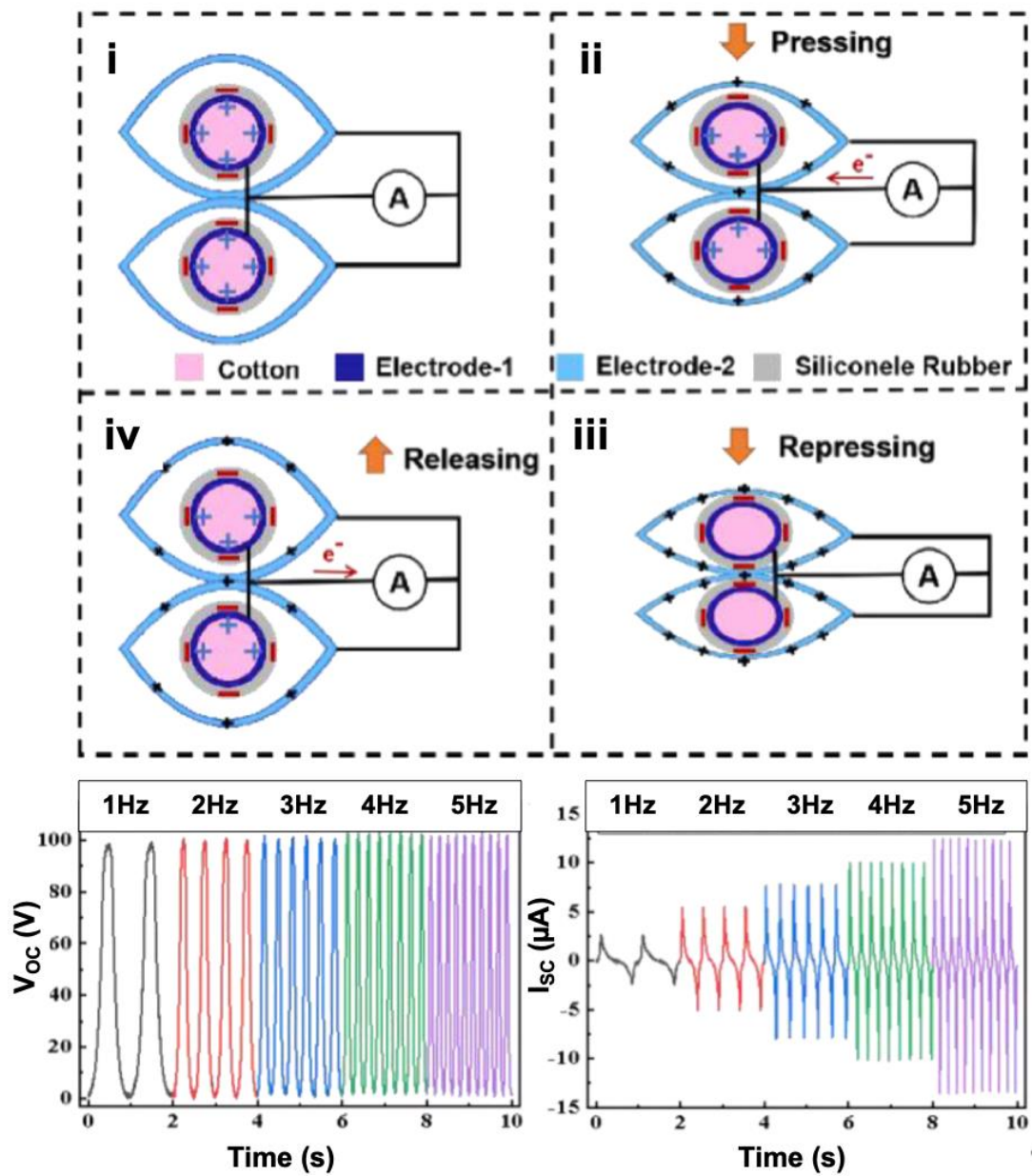


Figure 19 The overview of 3D angle-interlock of cotton composite yarn

Source: Enfang He. (2020). Composites Part B: Engineering p. 108244.

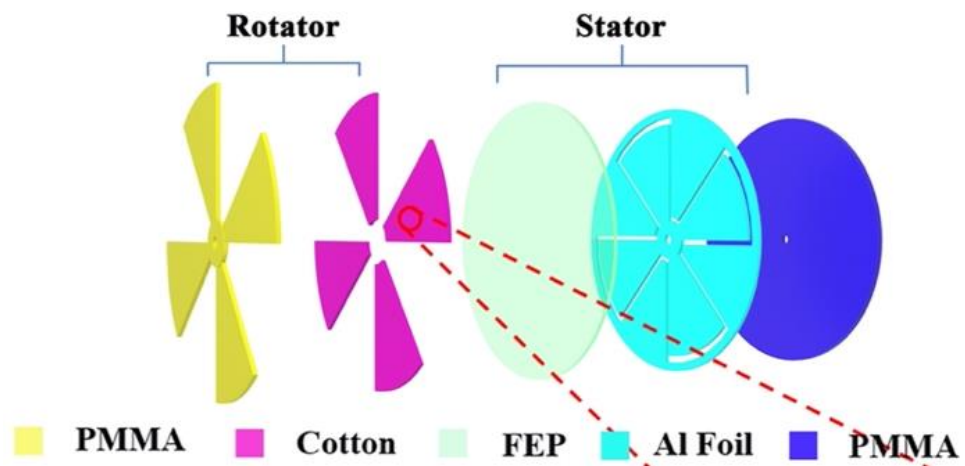


Figure 20 The wheel-shape designed of cotton-based TENG with FEP

Source: Xia R. (2022). Nano Energy p. 106685.

Table 1 The output efficiency of modified cotton-based TENG

| Tribo-positive material | Tribo-negative material | Modification methods       | $(V_{oc})$ | $(I_{sc})$   | Reference |
|-------------------------|-------------------------|----------------------------|------------|--------------|-----------|
| Cotton                  | PTFE                    | Surface modification       | 660 V      | 12.5 $\mu$ A | (15)      |
| Cotton                  | PTFE tubes              | Materials composite        | 557 V      | 26 $\mu$ A   | (16)      |
| Cotton                  | FEP                     | Structural design          | 789 V      | 8.9 $\mu$ A  | (18)      |
| Cotton/silver paste     | PTFE-coated fabric      | Materials composite        | 145 V      | 3.2 $\mu$ A  | (51)      |
| Cotton yarn             | PTFE                    | Structural design          | 900 V      | 19 $\mu$ A   | (53)      |
| Cotton/CO               | PTFE                    | Material composite         | 420 V      | 54 $\mu$ A   | (54)      |
| CN-silk                 | F-cotton                | Chemical functionalization | 217 V      | 50 $\mu$ A   | (14)      |

The summary of the output efficiency of modified cotton-based TENG in each literature was shown in Table 1. All the literature reported that the modified cotton-based TENG can generate high  $V_{oc}$  but the obtained  $I_{sc}$  is still low owing to the temporary charge generation. According to the triboelectric mechanism, while two materials contact and separate continuously, the charges are generated and can stay on each material surface for a while. When two materials separated, the charges have a chance to loss in surrounded that make the limitation in  $I_{sc}$  (19). Also, when the materials contacted or have some friction repeatedly, the waste heat then created and be another driving force to let the charges loss that were uncontrollable, as shown in Figure 21. Up to now, there are several methods to improve the TENG efficiency such as surface modification (20), chemical functionalization (21), structure design (22) and hybrid system modification *etc.* (23). In particular, the combination of energy harvesting mechanisms to harvest various kinds of energy sources within one device, known as the hybrid system, is in demand.

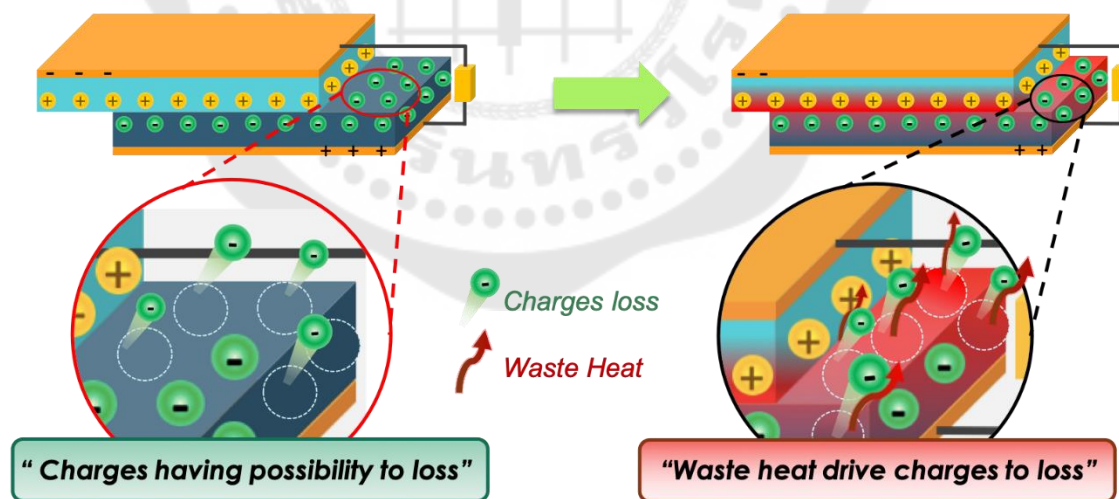


Figure 21 The effects of working mechanism of TENG

There are several kinds of hybrid systems such as hybrid triboelectric-thermoelectric nanogenerator (hybrid TENG-TEG) (24), hybrid triboelectric-photovoltaic nanogenerator (hybrid TENG-PV) (25), hybrid triboelectric-piezoelectric (hybrid TENG-

PENG) (26) and hybrid triboelectric-electromagnetic nanogenerator (hybrid TENG-EMG) (27). Y. Yang and *et.al.* fabricated hybrid TENG and TEG as energy cell for the first time (24). In 2016, Z. Wen and *et.al.* presented fiber-shaped based hybrid TENG and PV (25). In the same year, X. Chen and *et.al.* demonstrated hybrid TENG and PENG based on P(VDF-TrFE) nanofibers (26). X. Wang and co-workers reported a rolling hybrid TENG with EMG for harvesting blue energy (27). The variety of hybrid system was expanded to integrate TENG with other energy harvester by combine their working mechanism (29). Among them, the hybrid TENG-TEG get attention due to the ability of the TEG materials to convert thermal energy into electricity ). When a temperature gradient occurs, the charge carriers come across to the other side of TEG based on the Seebeck effect and generate the electrical output (28). Therefore, the waste heat can be solved and the high  $I_{sc}$  generation of TENG-TEG can be produced by simultaneous harvesting of mechanical energy and waste heat energy gaining from triboelectric mechanism (19).

## 2.6 Thermal energy harvester

The thermal energy harvester is the device that can captured thermal energy or temperature differences and convert to electrical energy known as thermoelectric nanogenerator (TEG) (55).

### 2.6.1 Thermoelectric nanogenerator (TEG)

The thermoelectric nanogenerator is the thermal energy harvester that could convert the thermal energy by the gradient of temperature and transform to electricity. The structure of TEG consists of p-type and n-type semiconductor materials connecting together with electrode. The materials contain the charge carriers of holes and electrons (29), as illustrated in Figure 22.

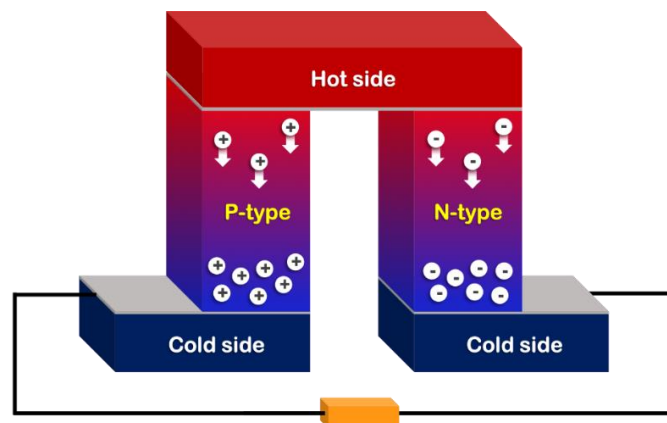


Figure 22 The structure of thermoelectric nanogenerator

Source: <https://schroedergroup.org/thermoelectrics/>

The working mechanism of TEG based on Seebeck effect that have been explained by Thomas Johann Seebeck in 1820, caused by the different of temperature related on absorbed and transferred heat (29). When heat is generated on one side of the thermocouple, the charge carriers will have enough energy to move towards to the cooler side. The different amount of charge carriers on each side resulting the opposite charged at both ends. The hot end side tends to be positivity charged while the cool end side present the negativity charged. Then, the electrical output is generated in a series circuit as shown in Figure 23.

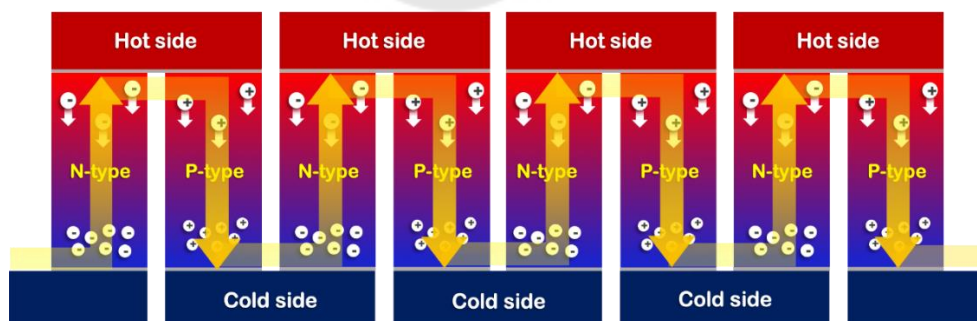


Figure 23 Working mechanism of thermoelectric nanogenerator

Source: Ssennoga Twaha. (2017). Energies p. 2016.

The electrical performance of TEG depend on three keys properties of high electrical conductivity but low thermal conductivity with good Seebeck coefficient to produce the ability of transform heat to electricity (56). The Seebeck coefficient relates to equation 1. by measuring the gradient of voltage with the responding of temperature gradient, where  $S$  is Seebeck coefficient,  $\Delta V$  is gradient of voltage and  $\Delta T$  is temperature gradient. Figure of Merit ( $zT$ ) of materials is also important to characterize the performance of TEG. According to Equation 2, the  $z$  is figure of Merit,  $T$  is the average temperature,  $\sigma$  is the electrical conductivity and  $K$  is the thermal conductivity (57).

$$S = \frac{\Delta V}{\Delta T}$$

Equation 1 Seebeck coefficient formula

$$zT = \frac{S^2 \sigma}{K} T$$

Equation 2 Figure of Merit formula

Thermoelectric materials can be separated into two types of conventional materials and new materials. Conventional TEG materials consist of bulk semiconductor alloys which separate into three group using the criteria from the temperature range of less than 150 °C, 150 °C to 500 °C and over 500 °C. The conventional materials such as Bismuth Telluride ( $\text{Bi}_2\text{Te}_3$ ) have  $zT$  of 1 at room temperature and Lead Telluride ( $\text{PbTe}$ ) normally contain the  $zT$  of 1.4-1.8 (55). The high  $zT$  of conventional materials present a high output efficiency. For new materials, consists of ceramic ( $\text{Ca}_3\text{CO}_4\text{O}_9$ ), metals

(Chalcogenide) and conductive polymers (55), they have a property of good electrical characteristic with low thermal conductivity.

### 2.6.2 Flexible thermoelectric nanogenerator (Flexible-TEG)

The fabrication of TEG for merging with e-textile system prefer the properties of wearable and flexible. However, the most highly efficient TEG materials are ceramics. Fabricating flexible TEG for e-textiles is normally tried to make the TEG in small pieces and embed it into flexible fabric. In 2014, K. Jin and et.al. were fabricated wearable TEG by screen printing  $\text{Bi}_2\text{Te}_3$  as n-type and antimony telluride ( $\text{Sb}_2\text{Te}_3$ ) as p-type thick film on glass fabric-based textile that act as a flexible supporter, according to Figure 24. The electrodes were laser by laser ablation for stretchable. The output efficiency in form of output voltage and power density generate about 90 mV and  $3.8 \text{ mW/cm}^2$  at a gradient temperature of 50 K (32).

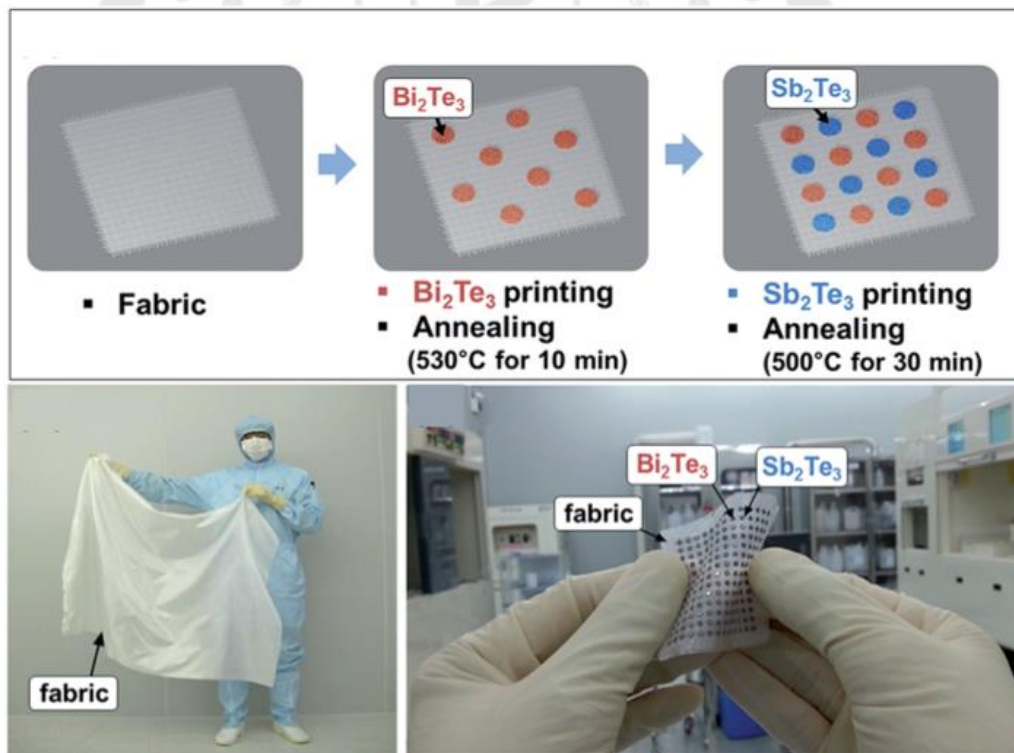


Figure 24 The overview of wearable TEG

Source: Kim S.J. (2014). Energy Environ Sci p. 1959.

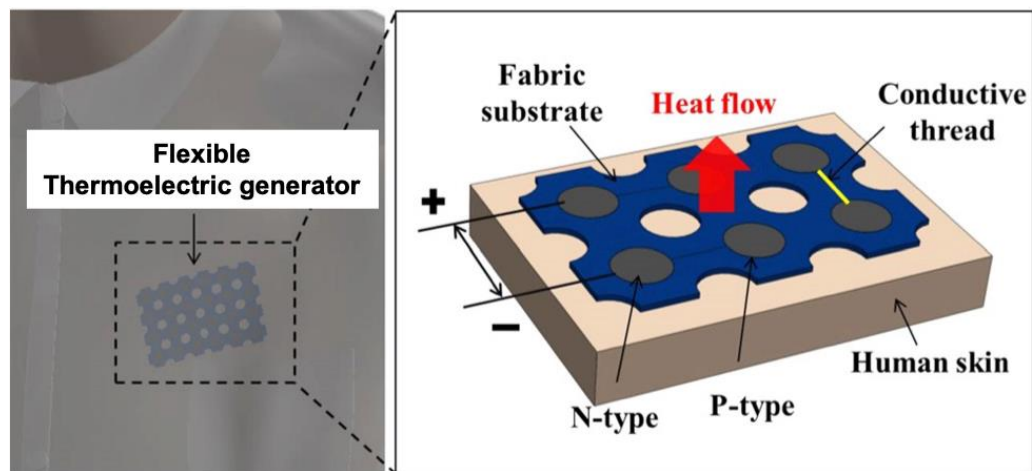


Figure 25 A schematic of the wearable TEG on the skin

Source: Kim MK. (2014). Smart Mater Struct p. 105002.

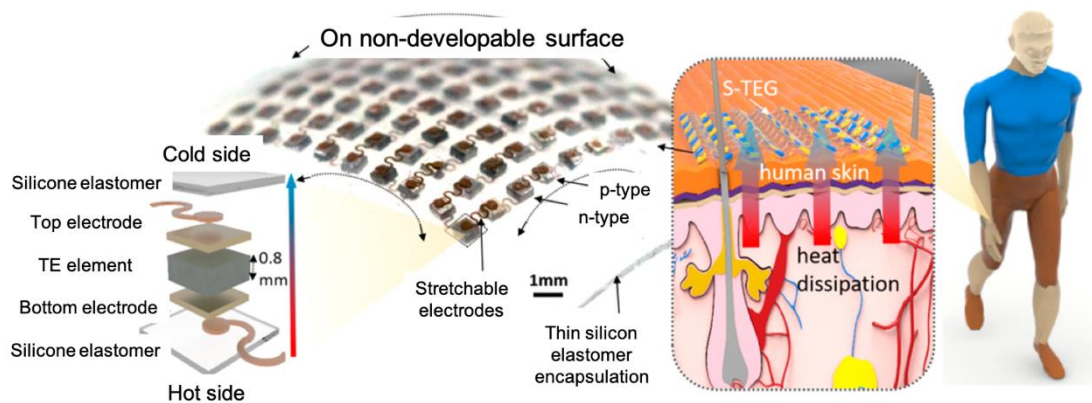


Figure 26 The structure and application of stretchable TEG

Source: Yang Y. (2020). Nano Lett p. 4445-53.

Also, K. Min-Ki and et.al. presented a wearable TEG that is designed to easily embedded in clothing. The p-type and n-type thermocouple are in the form of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  and  $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ , respectively. Both materials were prepared in the form of viscous printable ink to fill in the holes of the polymer-based fabrics substrate and

connected by silver thread as shown in Figure 25. This wearable TEG shows flexibility and suitable use with the human body. The output efficiency of output voltage, current and power of TEG device of 14.2 mV, 15.8  $\mu$ A and 224 nW, respectively, could be generated with a gradient of temperature about 15 K (33). Recently, in 2020, Y. Yang and *et.al.* reported a stretchable TEG by embedding  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  thermocouple as n-type and p-type materials. The TEG materials are connected by electrode and embedded on a silicone elastomer (Ecoflex) as shown in Figure 26. The stretchable TEG showed flexibility by attaching to human skin as wearable device for medication field. The overall output efficiency reaches about 117 mV, 5.4 mA and  $0.15 \text{ mW/cm}^2$  of output voltage, output current and output power density, respectively by harvesting a waste heat from human body with gradient temperature of 19.7 K (34). According to literature, the TEG fascinate to overcome the limitation of  $I_{sc}$ . Nevertheless, the solid conventional TEG materials that embedded on flexible substrate are limit their flexibility to only one direction. All flexible and stretchable materials in textiles-based hybrid TENG-TEG are challenges.

## 2.7 Hybrid triboelectric-thermoelectric nanogenerator (Hybrid TENG-TEG)

Hybrid triboelectric-thermoelectric (Hybrid TENG-TEG) is a combination of TENG and TEG in branch of materials, structure and the working mechanism. According to the literature, in 2018, Y. Wu and *et.al.* developed a 2D rotary-TENG hybrid with TEG by using nylon and polytetrafluoroethylene (PTFE) as tribo-positive and tribo-negative materials with using  $\text{Bi}_2\text{Te}_3$  as thermoelectric module. The structure of hybrid TENG-TEG (TTENG) was separated into two parts of rotator and stator as shown in Figure 27a. The electrical output performance was measured and showed a higher output voltage and current than that of the ordinary TENG, according to Figure 27b. Also, in Figure 27c, they confirmed the greater charge efficiency by 87% by comparing to ordinary TENG (29). In 2019, B. Seo and *et.al.* reported a hybrid TENG-TEG by using  $\text{Bi}_2\text{Te}_3$  and Polydimethylsiloxane (PDMS) as main materials and aluminum as electrode. The structure of the device was designed in a single-electrode mode with tiles-shape. The harvesting depends on one touch input as shown in Figure 28. The output efficiency of

$3.27 \mu\text{W}/\text{cm}^2$  was achieved that was higher than that of traditional TENG for 1.2 times (31).

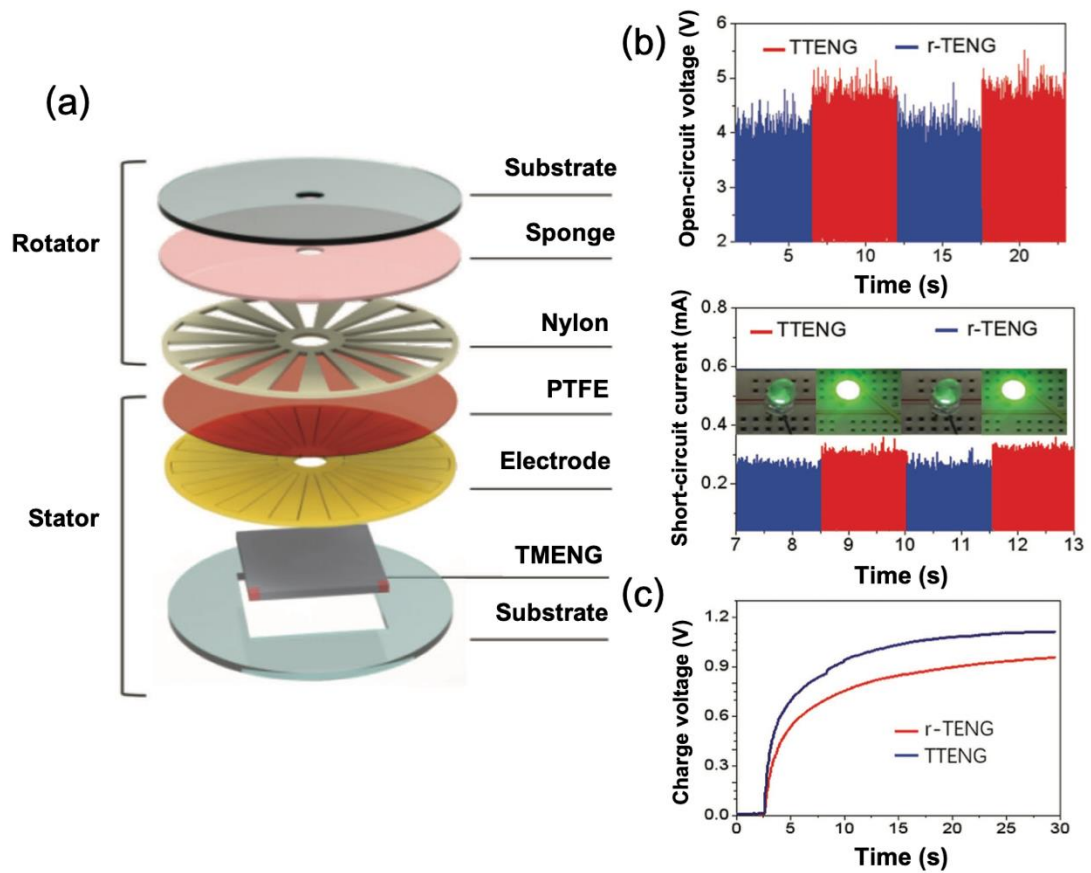


Figure 27 (a) The structure of TTENG (b) The output performance of TTENG and r-TENG (c) The charge efficiency of TTENG and r-TENG

Source: Wu Y. (2018). Advanced Materials Technologies p. 1800166.

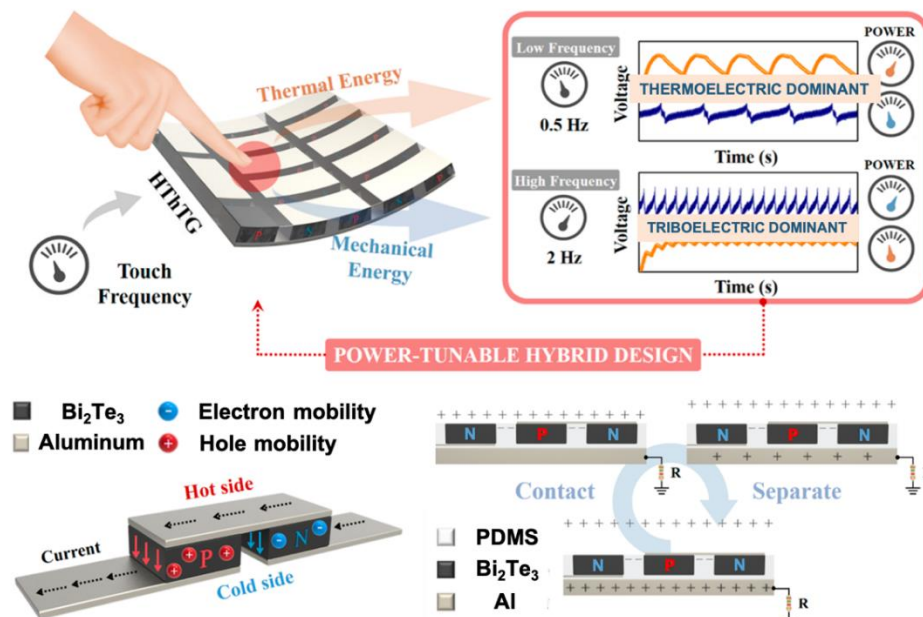


Figure 28 Overview of keyboard-designed hybrid TENG-TEG in a single-electrode mode

Source: Seo B. (2019). ACS Energy Lett p. 2069-74.

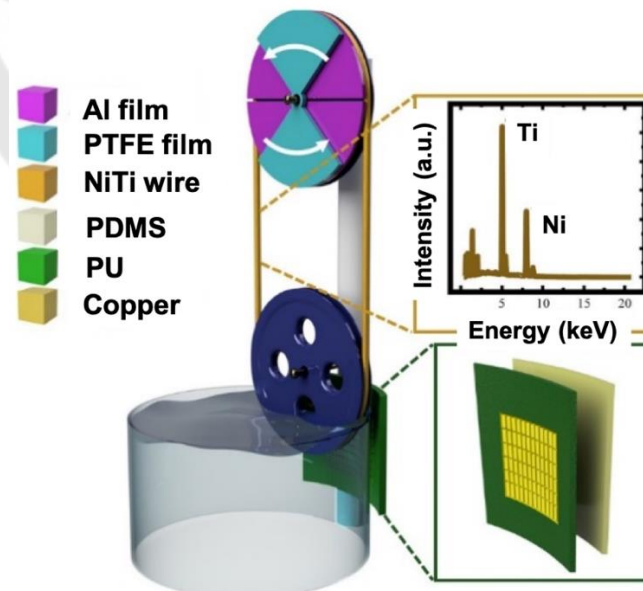


Figure 29 The structure of shape-memory alloy-based hybrid TENG-TEG

Source: Lee D. (2021). Nano Energy p. 105696.

Also, D. Lee and *et.al.* work, the hybrid device was separated into two parts. First, the TENG with disk-shape was fabricated by aluminum film and Teflon film while in the second part was used  $\text{Bi}_2\text{Te}_3$  pellets to act as thermoelectric materials by having the shape-memory alloy wire to connect each part and help in motion. The TEG device was designed in disk-shape structure, according to Figure 29. The output efficiency provides 73.17 V which is greater than that of 58.29 V from pristine TENG (30). However, the fabrication of hybrid TENG-TEG usually focused on structural design. i.e., disk shape (30) rotary shape (29), and tiles shape (31). Meanwhile fabric modification is still rare. By taking TEG into account, the fabrication of TEG for merging with e-textile system prefer the wearability and flexibility. So, the new materials of TEG in a group of conductive polymers are candidate, due to their flexibility, light weight, and excellent thermoelectric properties.

## 2.8 Conductive polymers

Conductive polymers are organic polymers that have electrical and optical properties. The molecular structure, which consists of sigma ( $\sigma$ ) bonds and alternate pi ( $\pi$ ) bonds in polymer backbone, are also known as conjugate polymer. Polyacetylene is the first type of conductive polymer that was discovered by Hideki Shirakawa and *et.al.* (58). The electrical conductivity of polyacetylene is generated when the electron can move freely across the polymer chain with delocalized orbitals.  $\sigma$ -bonds stored electrons of an atom to carry each atom together. While  $\pi$ -bonds which are part of double bonds also connecting each atom by attracting the electron above and below the molecular structure which present delocalized orbitals as shown in Figure 30.

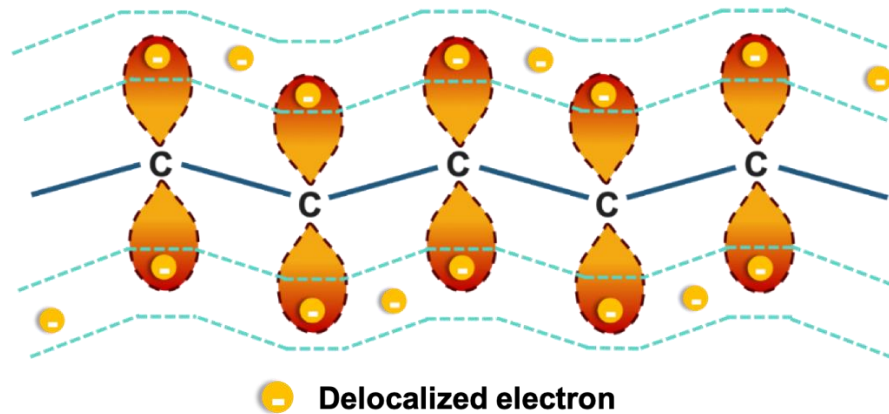


Figure 30 Polyacetylene molecular structure

Source: <https://youtu.be/UjMbwS0LOkU?si=1jae1RkVneYEnSho>

The mechanism of conduction for conductive polymers relates to the transportation of charge carriers. The charges carrier hops from one state of delocalized orbital to another delocalized orbital. For conductive polymers in thermoelectric system, the temperature is involved to explain the conductivity. Conductive polymers have a wide range of electrical conductivity which depends on the difference in temperature. Each of them has a specific temperature which can present excellent electrical conductivity. Also, the Mott model is in charge to explain the mechanism in conductive polymers. In this model, the dependence of temperature behavior on electrical conductivity can be described. The formula of Mott model that involves conductivity and temperature are in Equation 3, where  $n$  is dimensionality of charge transfer,  $\sigma_0$  is the electrical conductivity at room temperature and  $T_0$  is Mott's temperature constant (59).

$$\sigma = \sigma_0 \exp \left[ -\left( \frac{T_0}{T} \right)^{1/n+1} \right]$$

Equation 3 Mott's model formula

Also, to improve the efficiency of electrical conductivity, various processes can be achieved such as doping process, post treatment, energy-filtering effect, interfacial

ordering effect and structure design process. Among them, the doping process is commonly separating into n-type doping and p-type doping. According to Figure 31a, electronic structure is presented, it consists of HOMO energy band and LUMO energy band. The HOMO energy band is the highest energy level which filled lot of electrons while the LUMO energy band is the lowest energy level that no electron was contain. The doping process then occurs only when HOMO and LUMO energy band of the conductive polymer and dopants overlap together. For the n-type doping, when conductive polymer was doped by n-type dopants, the electron in the HOMO will hop to the LUMO of conductive polymer. While the p-type doping, the electrons in the HOMO of conductive polymer transfer to the LUMO of the p-type dopants, as shown in Figure 31b. Also, the doping process relates to an increasing and decreasing number of electrons. While increasing, the electrons were added to atom and created more orbital that lack of electron to have more space to move that present the n-type doping. While p-type doping, the electrons were removed to atom and created empty space in the valence orbital leading electron to move freely. So, the electron of polymers has the ability to move more easily while doping to create an easily transporting charges and generate more electrical current (60).

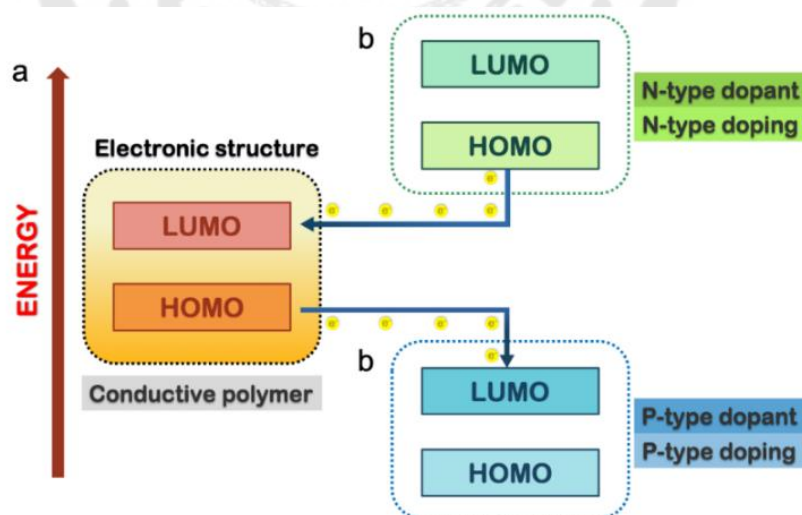


Figure 31 Electronic structure of (a) conductive polymer and (b) n-type and p-type dopants

Source: Yaun Wang. (2019). Advanced Materials p. 1807916. Conductive polymers or conjugate polymers are being adapted as thermoelectric materials. In addition, being flexible and lightweight, the conductive polymers are available represent thermoelectric properties by using at room temperature allowing to adapt with various structure design. Currently, Y. Zhang and et.al. were studied a various kind of polymers that qualified thermoelectric properties including polyacetylene (PAC), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), polythiophene (PT), poly(3-hexylthiophene) (P3HT) and Nafion (36, 37). Among them, P3HT and PANI are outstanding, bringing motivation for using in this work.

### 2.8.1 Poly(3-hexylthiophene) (P3HT)

Poly(3-hexylthiophene) (P3HT) is a kind of conductive polymer which present as p-type materials. The molecular structure of P3HT shown in Figure 33, the polythiophene chain connects with a short alkyl group. The excellent electrical properties at room temperature make P3HT commonly used in thermoelectric field (38). However, P3HT has high price limitations, so another type of conductive polymer like polyaniline are also get attention.

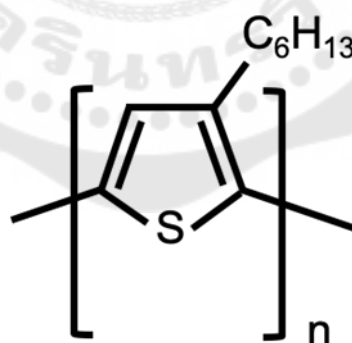


Figure 32 Molecular structure of poly(3-hexylthiophene)

Source: <https://www.researchgate.net/figure/P3HT-chemical-structure-23>

### 2.8.2 Polyaniline (PANI)

Polyaniline (PANI) is a widely used conductive polymer which acts as p-type materials that have low cost. PANI can be synthesized by aniline polymerization in form of powder. The molecular structure of PANI consists of an aromatic ring and nitrogen bridge as shown in Figure 32. The properties of environmental stability which can perform good electrical conductivity near room temperature, making them gain attention in a field of conductive polymers (37).

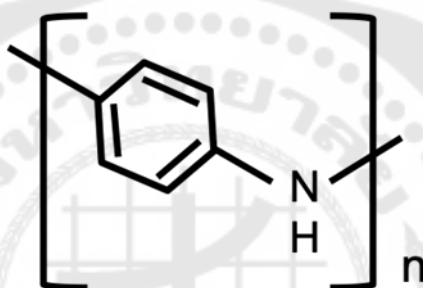


Figure 33 Molecular structure of polyaniline

Source: [https://www.researchgate.net/figure/Molecular-structure-of-polyaniline-PANI\\_fig1\\_328106467](https://www.researchgate.net/figure/Molecular-structure-of-polyaniline-PANI_fig1_328106467)

Due to their variety of processes to synthesis with the wide range of electrical conductivity nearby room temperature (36) that is suitable for collecting heat from human body by incorporating in e-textiles system. That makes PANI and P3HT get attention in TEG. Nevertheless, to develop the performance, adding carbon nanotubes (CNT) can help to increase electrical conductivity by assisting in electron transfer. In 2016, L. Wang and co-workers fabricated TEG device by using CNT/PANI films with dropping process as shown in Figure 34. This TEG composite film exhibited a high electrical conductivity of 1,440 S/cm which relates to the power factor of 217 mW/mK<sup>2</sup> that is 20 times higher than the power factor of TEG pure PANI films (39). Also, in 2021, S. Mardi and *et.al.* studied the thermoelectric properties of P3HT/CNT TEG device. This TEG showed the

high Seebeck coefficient of  $45.9 \mu\text{V/K}$  with high electrical conductivity of  $579 \text{ S/cm}$ . The output voltage and output current were measured and demonstrated about  $0.5 \text{ mV}$  and  $3 \mu\text{A}$ , while the pristine P3HT TEG shows the output voltage and output current of  $0.27 \text{ mV}$  and  $1.6 \mu\text{A}$ , which is 1.8 times lower than P3HT/CNT TEG (40). In comparison, the conductive polymers/CNT reveal higher output efficiency than that of the pristine conductive polymers. According to the electronic structure of PANI/CNT or P3HT/CNT as shown in Figure 35, while the conductive polymers have a driving energy, the electron in HOMO energy band has mobility to move to other energy level and leave the polaron. The polaron is placed on the fermi level, creating a narrow of energy gap to let the electrons jump to the LOMO energy band easily. The electrons were contained in LOMO energy band and move toward through CNT and export to the external load when having enough driving energy. The CNT helps the electrons to transfer to the external load easily. So, the conductive polymers could improve the electrical conductivity by composite with CNT.

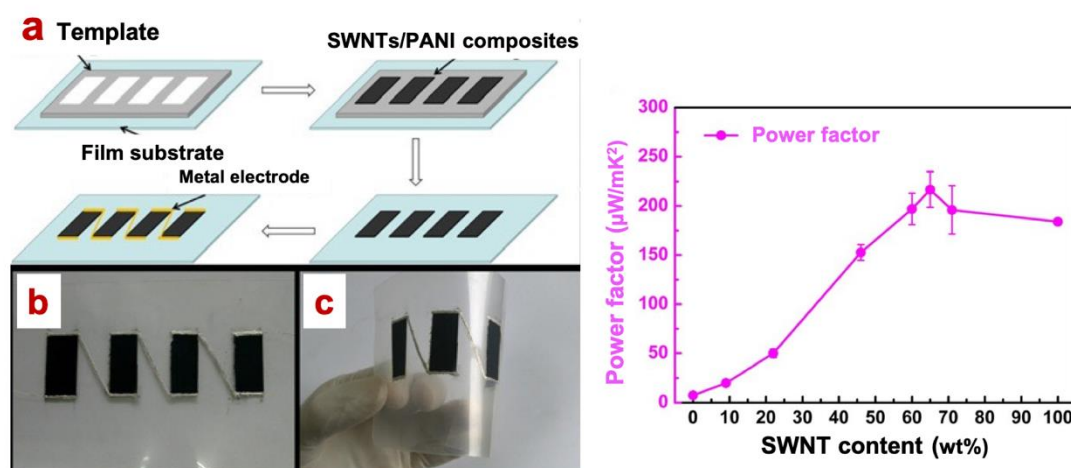


Figure 34 Fabrication method of CNT/PANI film and the power factor of TEG device

Source: Wang L. (2016). Chem Asian J. p. 1804-10.

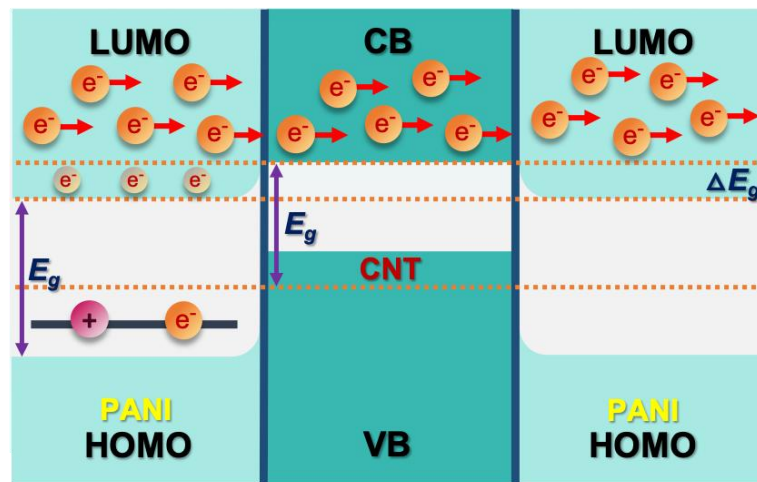


Figure 35 Electronic structure of conductive polymers/CNT

Here in this work, the materials modification was focused to fabricate hybrid TENG-TEG by using textiles as a substrate for flexibility where cellulose-based fabric including cotton and rayon act as tribo-positive materials and Teflon as tribo-negative materials. The cellulose-based fabrics were modified as three phase composites to improve the output efficiency of hybrid device. The fabrics were ultrasonicate dip-coated with conductive polymers as thermoelectric material of Poly(3-hexylthiophene) (P3HT) and polyaniline (PANI) composited with carbon nanotubes (CNT). The sliding-mode device is designed to generate sufficient heat and convert to highly efficient output. The surface morphology of fabrics and fabrics-conductive polymers/CNT were studied. The functional groups and fingerprints of fabrics and conductive polymers are analyzed. The 3D images distribution of conductive polymers/CNT inside fabrics are examined. Also, the effect of conductive polymers/CNT adding to the electrical properties and output efficiency, i.e., impedance, conductivity, output voltage, output current and output power of the hybrid triboelectric-thermoelectric nanogenerator (Hybrid-TENG-TEG) were investigated.

## CHAPTER 3

### RESEARCH METHODOLOGY

The fabrication of hybrid triboelectric-thermoelectric nanogenerator (Hybrid TENG-TEG) in this work is proposed by using cellulose-based fabrics as a tribo-positive and polytetrafluoroethylene (Teflon) as tribo-negative materials. The fabrics substrates were ultrasonicate dip-coated with three types of conductive polymers including Poly(3-hexylthiophene) (P3HT) and polyaniline (PANI) for compositing with carbon nanotubes (CNT). Thus, the fabrication process is separated into four sections of preparing the textiles, preparing conductive polymers, textiles dip-coating process and fabrication of hybrid TENG-TEG in sliding mode. The morphology, functional group, and chemical structure were characterized, and the electrical output efficiency was measured.

#### 3.1 Materials, equipment, and chemicals

##### 3.1.1 Materials and equipment

- 100 % rayon fabric (Bulliontex Co., Ltd.)
- 100% cotton fabric (Bulliontex Co., Ltd.)
- Polytetrafluoroethylene (commercial grade, Polytechindustry)
- Conductive Aluminum tape (RS Components Co., Ltd.)
- Acrylic sheets (RS Components Co., Ltd.)
- Spring (RS Components Co., Ltd.)
- Electrical wire (RS Components Co., Ltd.)
- Laboratory Glassware (DURAN LAB)
- Buchner
- Ultrasonic bath

##### 3.1.2 Chemicals

- Sodium chloride (ACS reagent 99%, Sigma Aldrich)
- Sodium hydroxide (ACS reagent 97%, Carlo Erba Reactifs SA)
- Calcium chloride (ACS reagent 99%, Sigma Aldrich)
- Nonionic surfactant (R&D grade, Sigma Aldrich)

- Aniline (ACS reagent plus 99%, Sigma Aldrich)
- Poly(3-hexylthiophene) (P3HT)
- Ammonium persulphate (APS)
- Hydrochloric acid (HCl)
- Chlorobenzene (AR 99.5 %, Loba Chemie PVT. Ltd.)
- Carbon nanotube (Nano Generation Co., Ltd.)

### 3.2 Textiles preparation

Before using commercial cellulose-based fabrics including cotton fabric and rayon fabric, cleaning processes are needed for appropriate uses.

#### 3.2.1 Desizing process of cellulose-based fabric

First, the cellulose-based fabrics were cut into rectangular shapes and weighted by balance. The desizing solution was prepared by dissolving 10 g/L of Sodium chloride (NaCl), 0.5 g/L of Calcium chloride ( $\text{CaCl}_2$ ) and 1 g/L of nonionic surfactant in clean water. The solution was boiled at 100°C until completely mixed. Afterwards, the cellulose-based fabrics were immersed into the solution for 45 min and rinsed with clean water several times. The fabrics were dried at room temperature as shown in Figure 36 before moving to the next step.

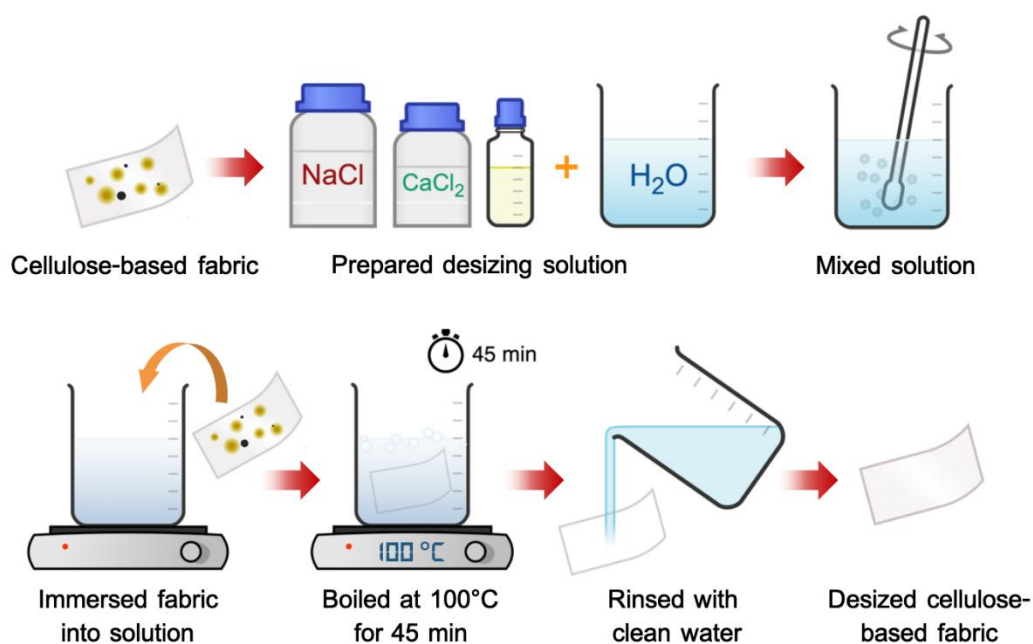


Figure 36 Desizing process of cellulose-based fabrics

### 3.2.2 Scouring process of cellulose-based fabric

The scouring solution was mixed by dissolving 4% of Sodium hydroxide (NaOH) with 0.2% of nonionic surfactant in clean water by dilution ratio 1:20 of reactant and water. The cellulose-based fabrics are then soaked in the solution at 95°C for an hour and rinsed with clean water. After completed scouring process, the fabrics were dried at room temperature as the process shown in Figure 37.

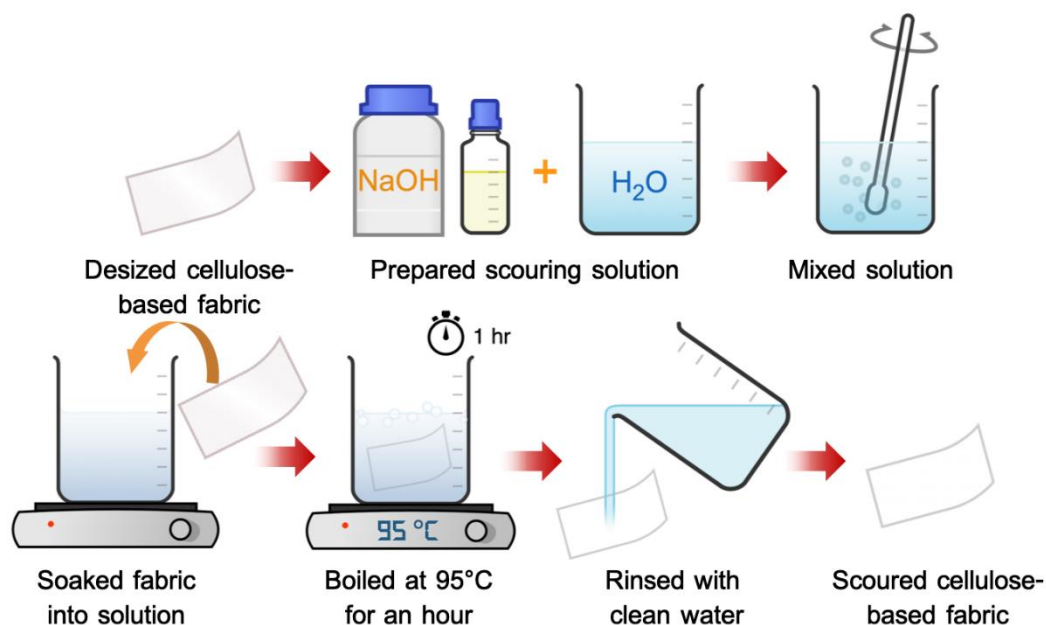


Figure 37 Scouring process of cellulose-based fabrics

### 3.3 Preparation of conductive polymers

Conductive polymers were prepared, including P3HT, PANI and PANI/CNT to be dip-coating materials for thermoelectric properties.

#### 3.3.1 Preparation of P3HT and P3HT/CNT solution

First, P3HT was grinded into fine powder to easily dissolve in solvent. The solution was prepared with three conditions of 50 mg, 100 mg and 150 mg of P3HT powder. The powder was dissolved into 40 ml of chlorobenzene (CB) solvent and stirred at 60°C by magnetic stirrer of 600 rpm for an hour to obtain the orange solution. Similarly, the P3HT/CNT solution was prepared in the same way with an additional of P3HT along with CNT, as depicted in Figure 38.

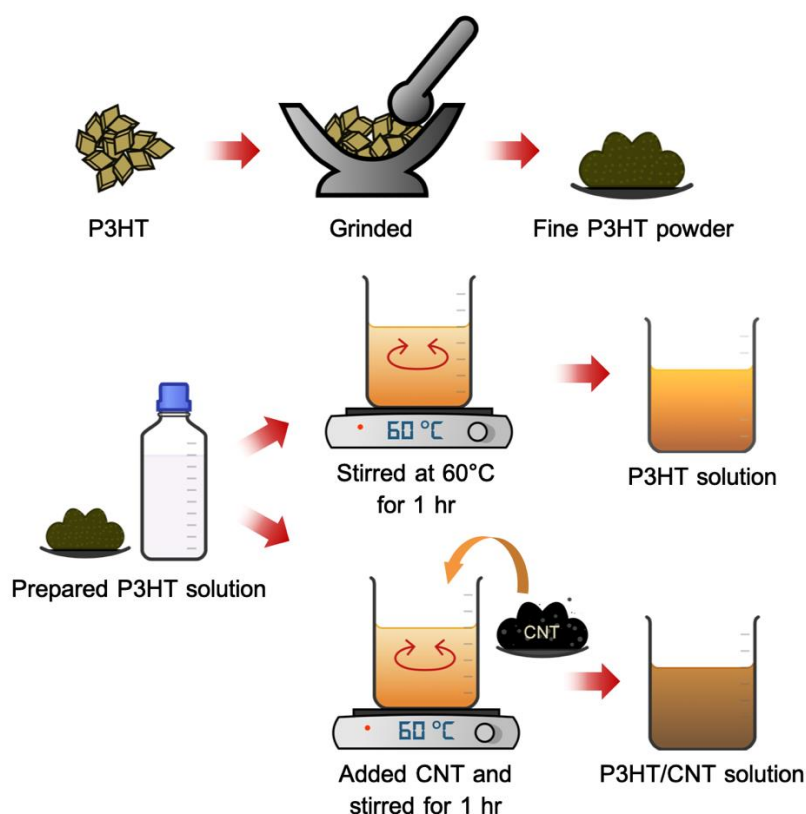


Figure 38 P3HT and P3HT/CNT preparation process

### 3.3.2 Synthesis of PANI and PANI/CNT

To synthesis PANI, the polymerization process occurred. As shown in Figure 39, 12 M hydrochloric acid (HCl) was diluted to be 1.5 M. First, the aniline solution was prepared, 10 ml of aniline were added to 125 ml of HCl and mixed by magnetic stirrer in an ice bath at below 5°C. Whereas for PANI/CNT synthesis, 6.81 g of CNT were added to aniline solution. Next, the ammonium persulphate (APS) solution was prepared by adding APS into 125 ml of 1.5 M HCl. An aniline solution was stirred continuously, the APS solution then constantly dropped 2-3 drops per second into the first solution to achieve the polymerization. Afterwards, the solution was stirred for 4 hours until completely mixed. The filtration of the solution occurred by 1.5 M HCl and deionized water until obtained the colorless filtrate with pH of 5. The precipitate substance was left for 24 hours and dried at 50°C for 12 hours to acquire the PANI/CNT powder. Then, the PANI and PANI/CNT solution was prepared with various conditions by

adding 0.05 g, 0.15 g, 0.25 g, 0.5 g and 0.75 g of PANI powder to 40 ml of deionized water. The PANI/CNT solution was also prepared by adding 0.05 g, 0.25 g, 0.50 g, 0.75 g, 1.00 g and 1.50 g of PANI/CNT powder to 40 ml of deionized water and mixed by magnetic stirrer for 30 min.

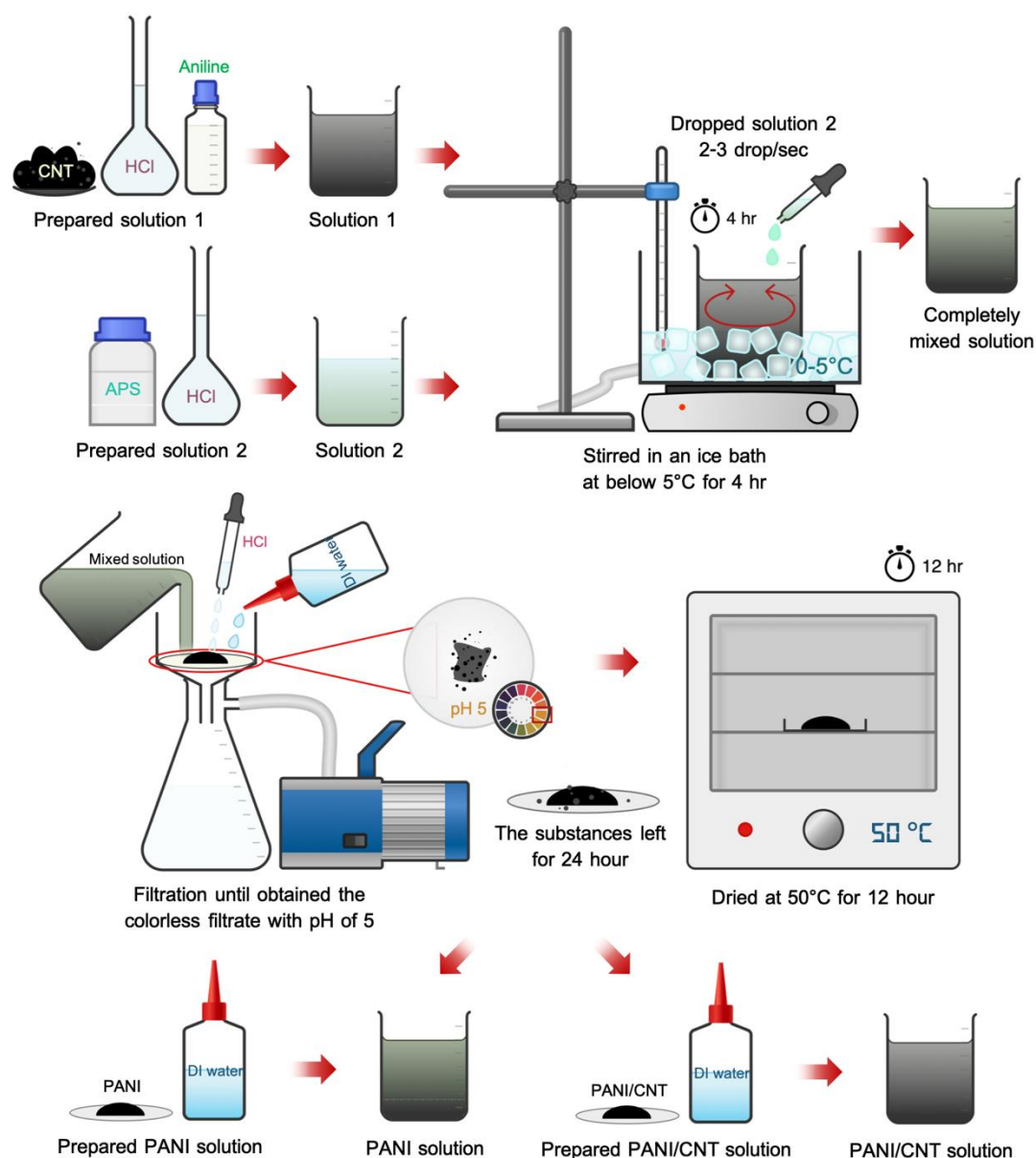


Figure 39 PANI and PANI/CNT synthesis process

### 3.4 Textiles dip-coating process

The cellulose-based fabrics including Rayon and cotton fabric were cut into  $3.5 \times 3.5 \text{ cm}^2$  and coated with P3HT conductive polymers. The prepared P3HT and

P3HT/CNT solution are contained in the beakers and were sonicated using ultrasonic bath for 30 min. Afterwards, the fabrics were dipped in the solution by continuously sonicate for an hour. The dip-coated fabrics were dried in oven at 60-70°C for 30 min. The process was repeated two times to receive Rayon/P3HT and Rayon/P3HT/CNT composite fabrics. Also, the cellulose-based fabrics/PANI composite have been prepared by dipping the Rayon and cotton into PANI and PANI/CNT solution with continuously sonicate for an hour. The dip-coated fabrics were dried in oven at 60-70°C for 30 min. The process was repeated two times as shown in Figure 40.

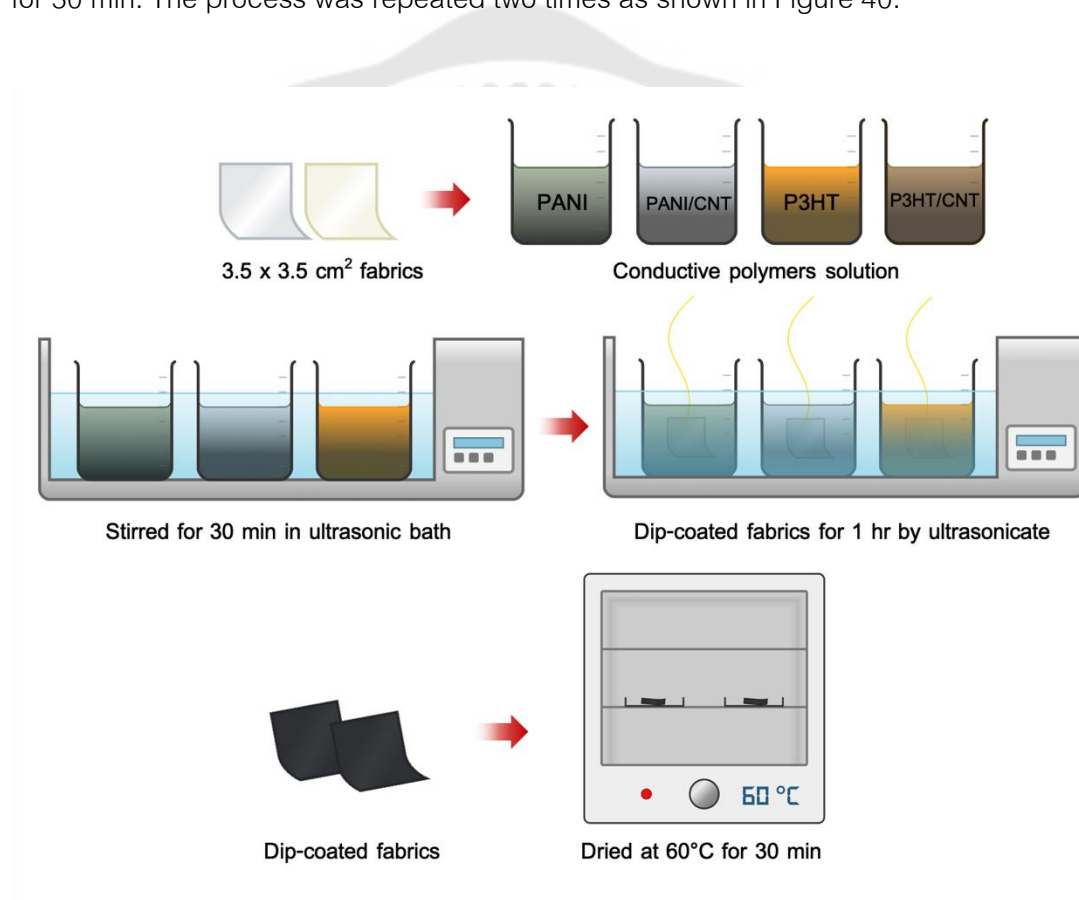


Figure 40 Textiles dip-coating process

### 3.5 Fabrication of hybrid TENG-TEG device

The hybrid TENG-TEG device was fabricated as three phase composites by using cellulose-based fabric of Rayon and cotton fabric as TENG substrate. Both fabrics were dip-coated with two types of conductive polymers of P3HT, P3HT/CNT, PANI and

PANI/CNT that act as thermoelectric materials. For the electrode part, glue fabric/CNT was selected for more flexibility and suitable use in textiles application.

### 3.5.1 Preparation of CNT electrode

As shown in Figure 41, the CNT electrode was prepared by mixing 0.15 g of CNT into 50 ml of deionized water while constantly stirred. The commercial glue fabrics were cut into  $3 \times 3 \text{ cm}^2$  and soaked in the CNT solution for 15 min and dried at room temperature. The soaking process was repeated 3 times more effectively before sprayed the acrylic spray to prevent the unadhered CNT.

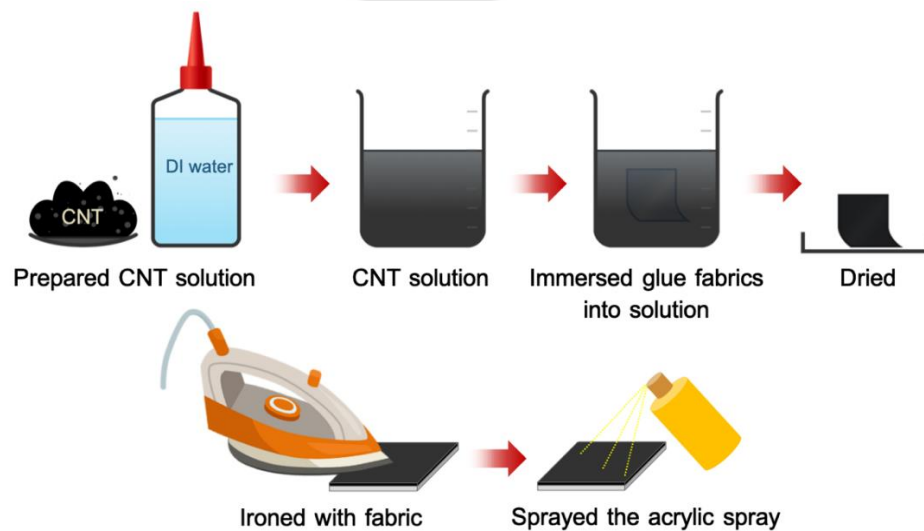


Figure 41 Preparation of CNT electrode

### 3.5.2 Fabrication of hybrid device

The fabrication of hybrid TENG-TEG device used cellulose-based fabrics including Rayon and cotton fabric as tribo-positive materials and Teflon as tribo-negative materials. The fabrics were composed with conductive polymers of P3HT, PANI and PANI composite CNT that act as thermoelectric materials. The prepared composite fabrics are then cut into square shapes of  $3 \times 3 \text{ cm}^2$ . The prepared CNT electrode was attached to fabric/conductive polymers as top electrode by ironed. Whereas aluminum tape was attached with Teflon as bottom electrode. Each electrode was connected with a wire for measuring electrical output efficiency under the working structure of sliding mode. The structure of hybrid TENG-TEG is shown in Figure 42.

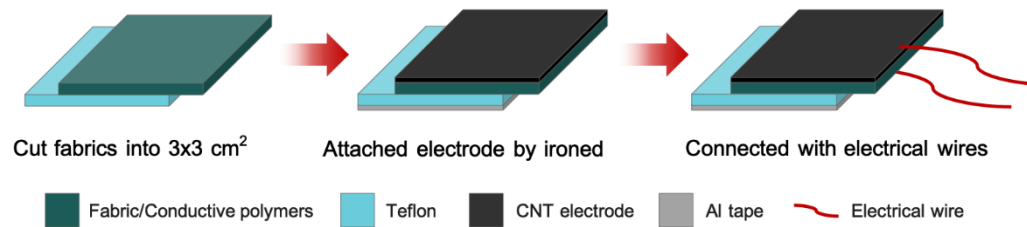


Figure 42 Fabricated hybrid TENG-TEG device

### 3.6 Characterization techniques

The morphology, functional group and chemical structures were characterized with different techniques and the electrical output efficiency was measured.

#### 3.6.1 The morphology characterization

The surface morphology of fabrics, conductive polymers and fabric/conductive polymers were observed by scanning electron microscopy (SEM) and light optical microscopy as in Figure 43 and Figure 44. For SEM technique, the samples were prepared within  $1 \times 1 \text{ cm}^2$  size and placed on the stub. The samples were coated with gold before characterization. For LOM, the samples were cut into  $3 \times 3 \text{ cm}^2$  sizes before focused by the light source.



Figure 43 The scanning electron microscopy (SEM)

Source: <https://cemas.osu.edu/capabilities/scanning-electron-microscopy-sem/quanta-200-sem-formerly-produced-fei>



Figure 44 Light optical microscopy (LOM)

Source: <https://www.leica-microsystems.com/science-lab/microscopy-basics/optical-microscopes-some-basics/>

### 3.6.2 The composite distribution visualization

The 3D visualization of conductive polymers/CNT dispersion inside fabrics phase was examined by Synchrotron radiation X-ray tomographic microscopy (SR-XTM) as shown in Figure 45. The projection of X-ray can visualize the difference of each phase of the samples which have difference of mass and density, creating the 3D images to confirm the composites.



Figure 45 Synchrotron radiation X-ray tomographic microscopy (SR-XTM)

Source: <https://www.slri.or.th/en/bl1-2w.html>

### 3.6.3 The chemical structure characterization

The functional group of fabrics, conductive polymers and fabric/conductive polymers/CNT were examined by using Attenuated Total Reflectance Fourier transform Infrared spectroscopy (ATR-IR), as shown in Figure 46. The samples were cut into the square shape of  $1 \times 1 \text{ cm}^2$ . The results of IR were shown molecular vibration within wavenumber between  $4000$  to  $700 \text{ cm}^{-1}$  that can investigate the functional group of the substance.

Also, the molecules of fabric/conductive polymers/CNT were identified to confirm the existence of the composite and the fingerprint of fabrics and conductive polymers by using Raman spectroscopy (Raman) as shown in Figure 47 and the samples were prepared in  $1 \times 1 \text{ cm}^2$ . The results of Raman showed a strong symmetry molecular vibrational while FTIR shown an asymmetry molecular vibrational.



Figure 46 Fourier transform Infrared spectroscopy

Source: <https://www.lqa.com/instrument/bruker-alpha-ii-ftir-spectrometer/>



Figure 47 Raman spectroscopy

Source: <https://www.bruker.com/en/products-and-solutions/infrared-and-raman/raman-spectrometers/what-is-raman-spectroscopy.html>

#### 3.6.4 The electrical properties of hybrid device

The electrical properties including impedance, conductivity and resistivity were examined by using a precision LCR meter (HP-4284A, Hewlett-Packard,

Palo Alto, CA). The cellulose/conductive polymer composite samples were measured at the frequency range of 100 to 1MHz by varying the temperature between room temperature up to 100°C to investigate the impedance, conductivity and resistivity of hybrid device.



Figure 48 The diagram of LCR meter

### 3.6.5 The electrical output measurement of hybrid device

The electrical output efficiency including  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  of composite fabrics were measured by using energy harvesting automatic compressing machine that relies on compressed force for contact-separation working mode and energy harvesting automatic sliding machine for sliding working mode, as shown in Figure 48a and b, respectively. The hybrid device was placed on the sample holder and the energy harvesting testing was tested by applying the force with using automatic sliding machine and connected to an oscilloscope (DSO-x 2012A, Keysight), and a digital multimeter (DMM, DM3058E, Rigol) as shown in figure 48c and d, to investigate the output voltage, output current and output power.

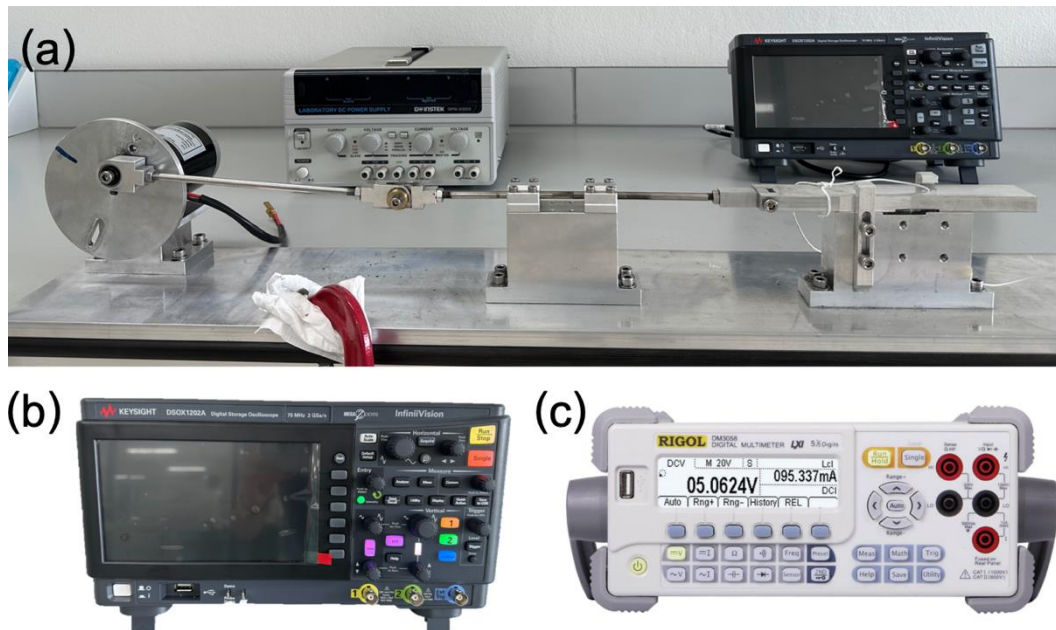


Figure 49 The diagram of energy harvesting machine of (a) sliding mode and electrical measurement of (b) oscilloscope (DSO-x 1202A, Keysight) and (c) a digital multimeter (DMM, DM3058E, Rigol)

Source: <https://www.conrad.com/p/rigol-dm3058-bench-multimeter-digital-cat-ii-300-v-display-counts-200000-40>

## CHAPTER 4

### RESULTS AND DISCUSSIONS

In this work, the fabricated hybrid TENG-TEG based on cellulose-based fabric/conductive polymers composites are separated into two categories, consisting of cellulose-based fabric/P3HT and cellulose-based fabric/PANI. In this chapter, the results and discussions are started with Rayon/P3HT and Rayon/P3HT/CNT following by Rayon/PANI, Rayon/PANI/CNT, cotton/PANI and cotton/ PANI/CNT systems. In each system, physical properties, surface morphology, filler distribution and chemical structure characterization is illustrated and explained. The characterization for conductive polymers is also mentioned. Since various amounts of conductive polymer are used, their explanation relative to the thermoelectric properties, electrical properties and electrical output efficiency are reported and discussed. The practical applications of the hybrid TENG-TEG for real-time driving portable devices *i.e.*, digital watch and safety flashing light are proposed. Moreover, the author does not propose only experimental results but also discuss scientifically of mechanistic insight during hybrid system operation based on the crucial role of conductive polymers incorporating for achieving high efficiency. The detailed discussion is illustrated in the final part of this chapter.

#### 4.1 Rayon/P3HT composite fabric system

According to cellulose-based fabric/P3HT system, the Rayon fabric was selected firstly to be composited with P3HT for hybrid TENG-TEG device's fabrication. The results and discussions are reported by starting with the characterization of P3HT powder, followed by Rayon and Rayon/P3HT composite fabric. The morphology characterization was performed by LOM and SEM. The IR and Raman techniques were used to confirm the chemical structure characteristic.

#### 4.1.1 Characterization of P3HT powders

The commercial P3HT powder was characterized by various techniques. The morphology of P3HT powder was observed by digital images, LOM and SEM technique. Additionally, the chemical structural characteristic was performed by ATR-IR and Raman.

##### 4.1.1.1 Morphological characterization of P3HT powders

The digital image in Figure 50 demonstrates the P3HT powders that are poured on filter paper in the form of coarse powders. The image was zoomed in, as can be seen in an inset of Figure, to show the dark purple color of P3HT powder. The morphology was observed by SEM and the SEM images are clearly shown in Figure 51a-b. The results reveal several small oval-shape particles with some incomplete spherical-shape connected in network. As also reported in Fokotsa V. and co-workers work, the P3HT morphology show small oval particles over the GO-sheet surface (61). The increasing of magnification at 50000x (Figure 51b) clearly demonstrates the agglomeration of each particle forming the secondary particles with an irregular shape within micron size.

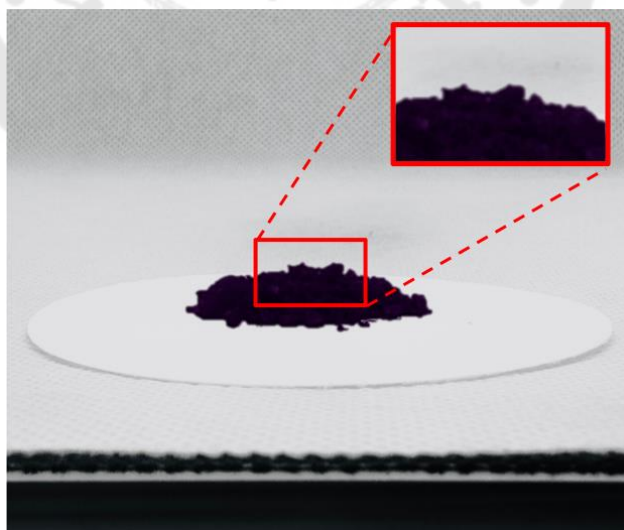


Figure 50 The digital images of P3HT powder

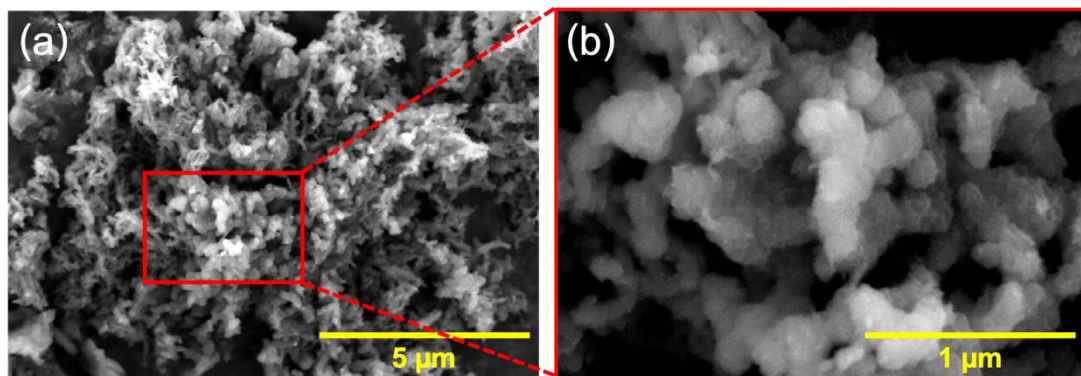


Figure 51 The SEM images of P3HT powder with magnification of (a) 10000x and (b) 50000x.

#### 4.1.1.2 The chemical structure characterization of P3HT powders

In addition to the morphological study, the functional groups and chemical bonding characteristics to identify the P3HT molecular structure were investigated by ATR-IR and Raman techniques. The results are displayed in Figure 52-53. According to Figure 52, the ATR-IR spectra is shown in a region of  $3500\text{--}700\text{ cm}^{-1}$ . All of the ATR-IR peaks matching with chemical bonding of P3HT molecules are summarized in Table 2. The presence of asymmetry  $\text{CH}_3$  aliphatic stretching vibration is observed at  $2920\text{ cm}^{-1}$ . The peaks at  $2870\text{ cm}^{-1}$  and  $2800\text{ cm}^{-1}$  correspond to the stretching vibration of symmetry  $\text{CH}_2$  aliphatic structure. The thiophene ring in P3HT molecular structure is presented by the detecting of evident  $\text{C}=\text{C}$  stretching vibration peak at  $1390\text{ cm}^{-1}$  (62). The band at  $1310\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  are assigned to the bending vibration of  $\text{C-H}$  and  $\text{C-S}$  group (63). All of the present peaks correspond to the characteristic of P3HT molecular structure. According to previous research by G. Kalonga et.al., the presence of IR spectrum for P3HT have been reported (64), which consistent to all peaks represented in Figure 52 as discussed above. Thus, the P3HT structure is confirmed. To double check the characteristics of P3HT, Raman technique is analyzed. As shown in Figure 53, the Raman spectra are reported within the  $500\text{--}3500\text{ cm}^{-1}$  range. The three peaks are particularly focused at  $500\text{--}2000\text{ cm}^{-1}$ , which can be confirmed to the existence of quinoid ring in P3HT molecule. Two peaks at  $760\text{ cm}^{-1}$  and

1430  $\text{cm}^{-1}$  are assigned to stretching vibration of C-S-C and symmetric C=C (65). Moreover, a small peak at 1330  $\text{cm}^{-1}$  belong to C-C intra-ring stretching (66). The observed Raman shift matched with chemical bonds is listed in Table 3. All the Raman peaks observed in this work are also consistent with the report from G. M. Paternò *et. al.* for illustrating P3HT characteristic (65). Raman technique can therefore support the results from ATR-IR to confirm the P3HT's chemical structure in this work.

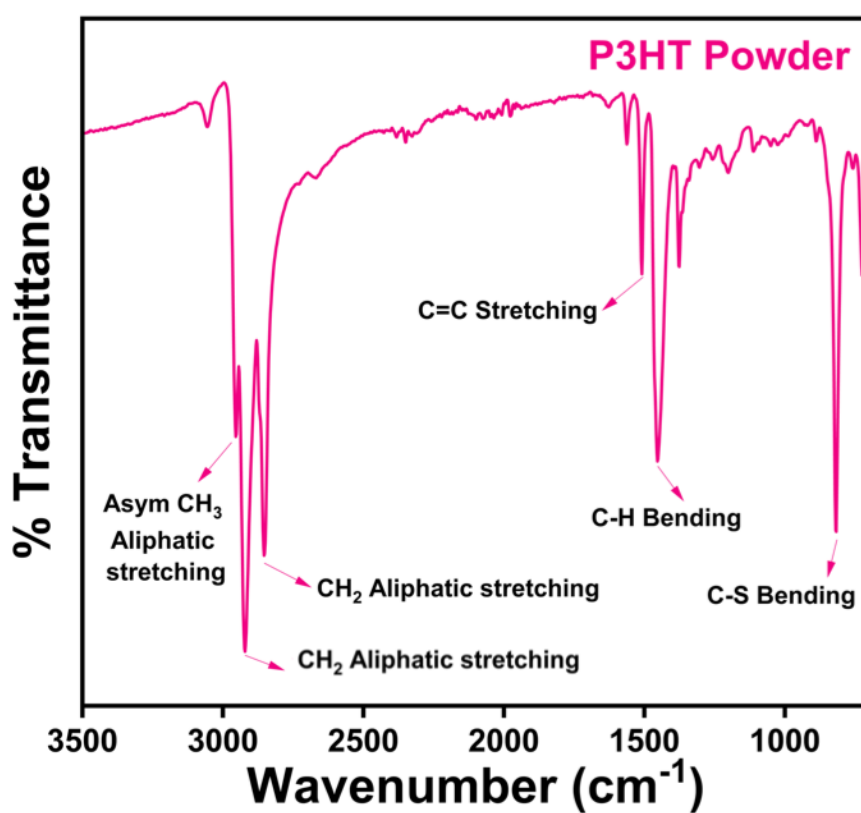


Figure 52 ATR-IR spectra of P3HT powders

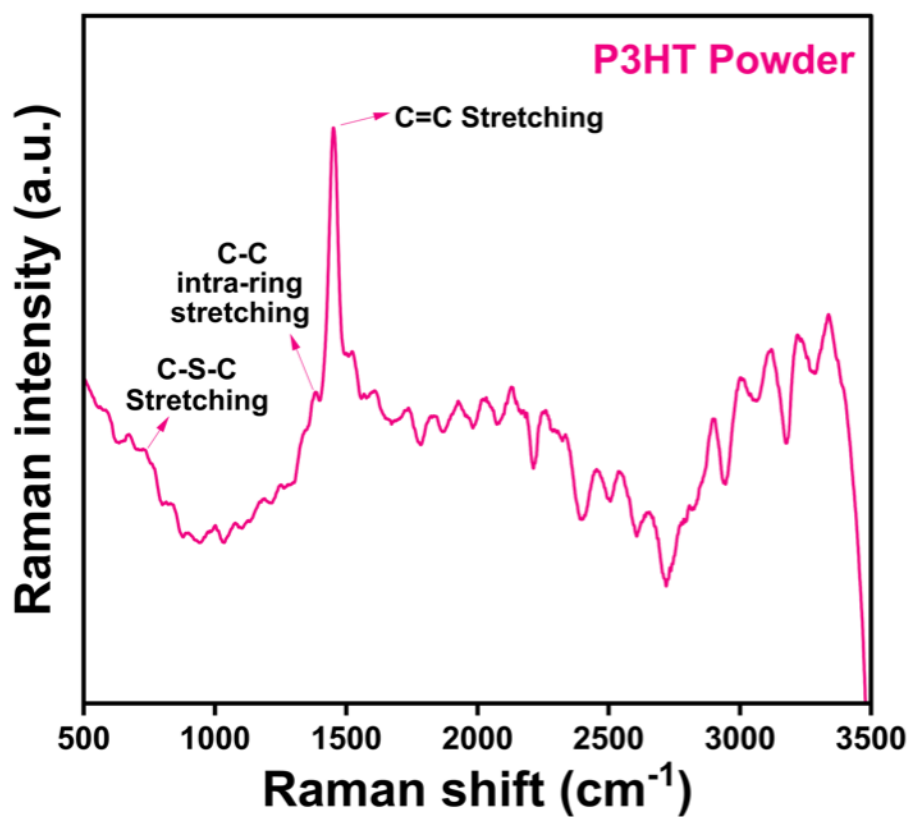


Figure 53 Raman spectra of P3HT powder

Table 2 The ATR-IR peaks identification list of P3HT

| Wavenumber (cm <sup>-1</sup> ) | Characteristic bond                            |
|--------------------------------|------------------------------------------------|
| 2920 cm <sup>-1</sup>          | Asymmetry CH <sub>3</sub> aliphatic stretching |
| 2870 cm <sup>-1</sup>          | CH <sub>2</sub> aliphatic stretching           |
| 2800 cm <sup>-1</sup>          | CH <sub>2</sub> aliphatic stretching           |
| 1390 cm <sup>-1</sup>          | C=C stretching                                 |
| 1310 cm <sup>-1</sup>          | C-H bending                                    |
| 680 cm <sup>-1</sup>           | C-S bending                                    |

Table 3 The Raman peaks identification list of P3HT

| Raman shift ( $\text{cm}^{-1}$ ) | Characteristic bond       |
|----------------------------------|---------------------------|
| 760 $\text{cm}^{-1}$             | C-S-C stretching          |
| 1330 $\text{cm}^{-1}$            | C-C intra-ring stretching |
| 1430 $\text{cm}^{-1}$            | C=C stretching            |

#### 4.1.2 Characterization of Rayon/P3HT composite fabrics

After the morphology and chemical structural of P3HT powder were characterized, the Rayon fabric composite with conductive polymers of P3HT powder within various conditions were prepared by ultra-sonication process. In the experiment, the physical and chemical characteristics of Rayon fabrics and Rayon fabric composited with P3HT could be examined by portable color spectrophotometer, LOM, SEM, IR, Raman and XRD techniques. Therefore, the discussion in the next part will consist of physical properties, surface morphology, composite distribution and chemical functional groups of Rayon fabrics comparison with Rayon/P3HT.

##### 4.1.2.1 Morphological characterization of Rayon fabric and Rayon/P3HT composite fabrics

The digital images of Rayon fabric and Rayon/P3HT fabrics in various condition between 50, 100 and 150 mg of P3HT are displayed, as shown in Figure 53. The Rayon fabric demonstrates a natural white color, while the Rayon/P3HT shows a purple color with different shades. The color shade is more intense from 50 mg to 150 mg condition depending on an increase of P3HT content, which can be assumed that the P3HT could be attached to the Rayon fabric by dip-coating process. For more scientific discussion, the measurement of the lightness values of fabrics was taken to account by portable color spectrophotometer. The results are present in  $L^*$ ,  $a^*$  and  $b^*$  values which are labeled in Table 4, where the  $L^*$  acts as a lightness value from 0 to 100 scale. The  $a^*$  value represents a color of green (negative value) to red (positive value) while the  $b^*$  value are the range of blue (negative value) to yellow (positive value) (67).

The largest  $L^*$  of about 94.5 is contained by Rayon fabric, representing purity without any composite of the fabric. According to Rayon/P3HT fabric, the  $L^*$  value was recorded at 49.0, 44.8 and 36.9 of Rayon/P3HT-50, 100 and 150 mg, respectively. The results show that the  $L^*$  value decreased relatively with an increase of P3HT content which relates to the different intense by eyesight, as shown in Figure 54a. In addition, Rayon/P3HT for all conditions showed the result in positive value of  $a^*$  and negative value of  $b^*$  demonstrating a range of red and blue color. Both  $a^*$  and  $b^*$  values represent the purple color that correlate to the color of this composite fabric. Figure 54b-c illustrates the flexibility of pristine Rayon fabric and Rayon/P3HT fabric. It is clearly shown that the Rayon and Rayon/P3HT fabrics can be folded, rolled up and twisted by showing capability to return to the initial shape.

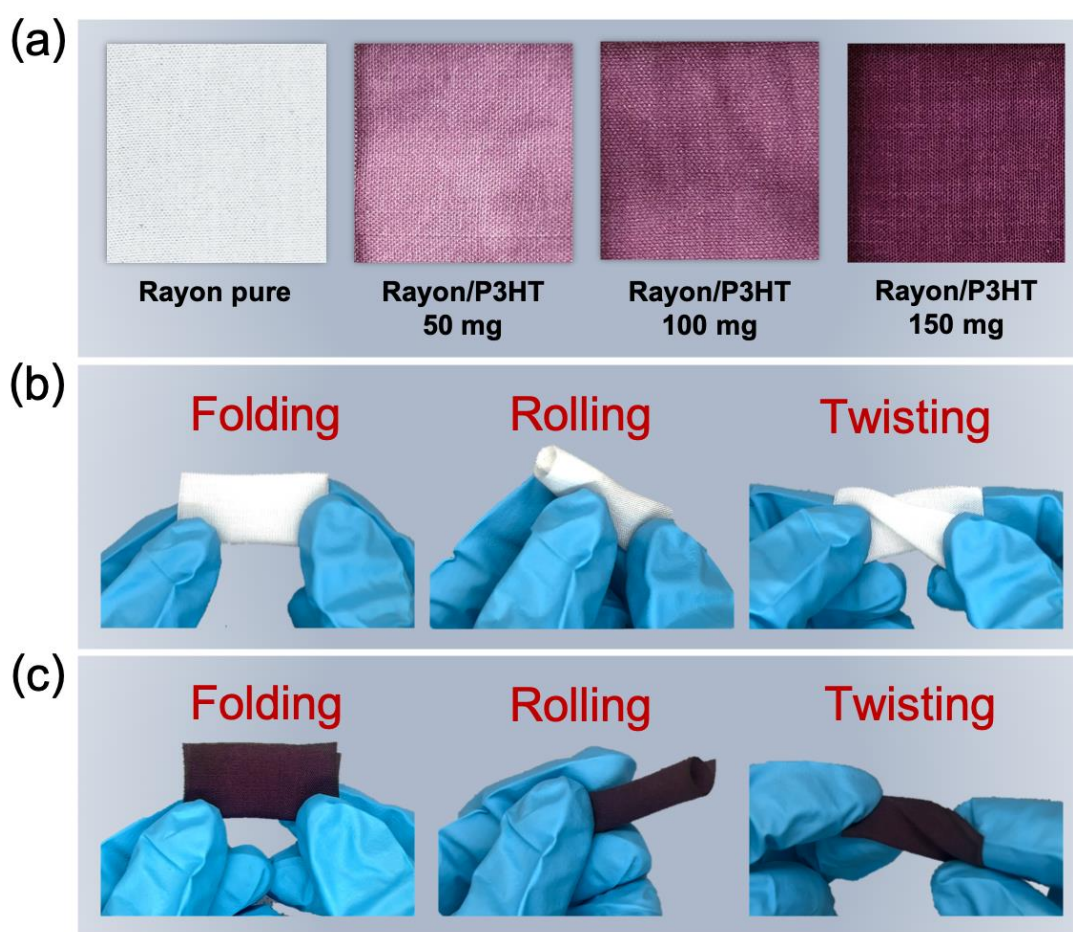


Figure 54 The digital images of (a) Rayon fabric and Rayon/P3HT in various condition of 50, 100 and 150 mg. The flexibility of (b) pristine Rayon fabric and (c) Rayon/P3HT.

Table 4 color measurement values of Rayon fabric and Rayon/P3HT fabric

| Fabric       | P3HT content (mg) | D65  |      |      |
|--------------|-------------------|------|------|------|
|              |                   | L*   | a*   | b*   |
| Rayon fabric | 0 mg              | 94.5 | 0.6  | -3.4 |
|              | 50 mg             | 49.0 | 13.0 | -6.0 |
|              | 100 mg            | 44.8 | 14.5 | -6.7 |
|              | 150 mg            | 36.9 | 14.1 | -7.0 |

The surface morphology of Rayon fabric and Rayon/P3HT in various conditions was observed by LOM, according to Figure 54, which consists of two parts. It demonstrates an orderly arrangement of Rayon fiber with a regularly weaving pattern as represented in dark yellow color. Other than that, some of porous occurred between each weaving pattern which could be observed at darker part within dark brown color. As the P3HT content is increased from 50-100 mg, the LOM image of the fabrics shows a decrease in the lightness as can be seen in Figure 55a-d, which corresponds to the digital images in Figure 54a and L\* value in Table 4. To analyze more specific surface morphology, the SEM technique is invited. The SEM images of Rayon fabric with different content of P3HT can be seen in Figure 55a-d. The pristine Rayon fabric demonstrates a bunch of small fibers weaving together in an orderly arrangement. The Rayon fiber's diameters are measured by using ImageJ software. It shows an average diameter of  $13.4 \pm 0.57 \mu\text{m}$  with a striated surface, according in Figure 56a. Meanwhile, the SEM images of Rayon/P3HT in various condition of 50, 100 and 150 mg in Figure 56b-d show that the surface of the fabrics have some small particles packing in between each fiber relative with a larger content of P3HT powder. The results can be assumed that the P3HT powder was successfully dispersed on the surface of Rayon. The energy dispersive spectroscopy (EDS) analysis was further used to confirm the elemental components of the P3HT particles on the surface of fabrics. The results of element mapping images with detection graph of carbon (C), oxygen (O) and Sulfur (S) are presented in Figure 57a-b. The mapping image of C, O and S is illustrated with red,

green and orange color, respectively. The EDS analysis results of pristine Rayon fabric can identify only the O and C atoms within 52.13 and 47.87 wt% (Figure 57a), which correlates to the containing of OH-group and C-H side chain in its chemical structure. The decreasing weight ratio for O element with an increasing of C takes place in Rayon/P3HT composite (Figure 57b) due to the presence of P3HT. Adding 150 mg P3HT in Rayon fabric resulted in the appearance of O and C at around 36.78 and 63.22 wt%. The S atom was found evidently at 1.83 wt%, which correlates to the S atom containing in thiols group of P3HT molecular structure. Therefore, the EDS analysis can be used to support SEM images to confirm a successful dispersion of P3HT on the Rayon fabric.

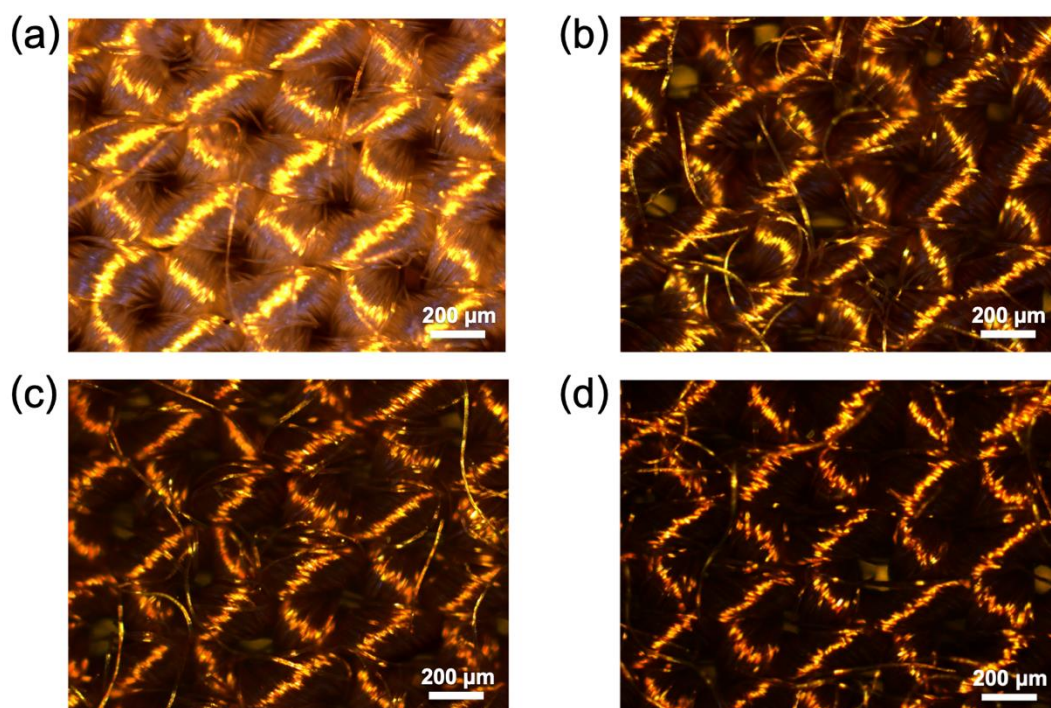


Figure 55 The light optical microscopy at 50x magnification of (a) Rayon fabric compare with Rayon/P3HT (b) 50 mg (c) 100 mg and (d) 150 mg.

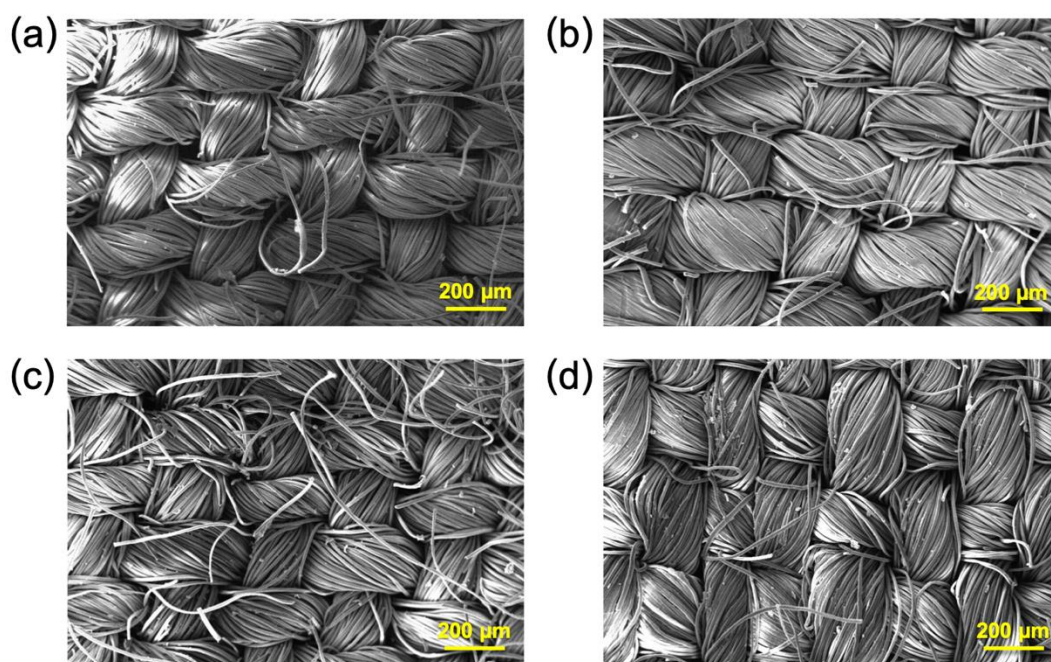


Figure 56 The SEM images of (a) Rayon fabric and Rayon/P3HT (b) 50 mg (c) 100 mg and (d) 150 mg at 75x magnification.

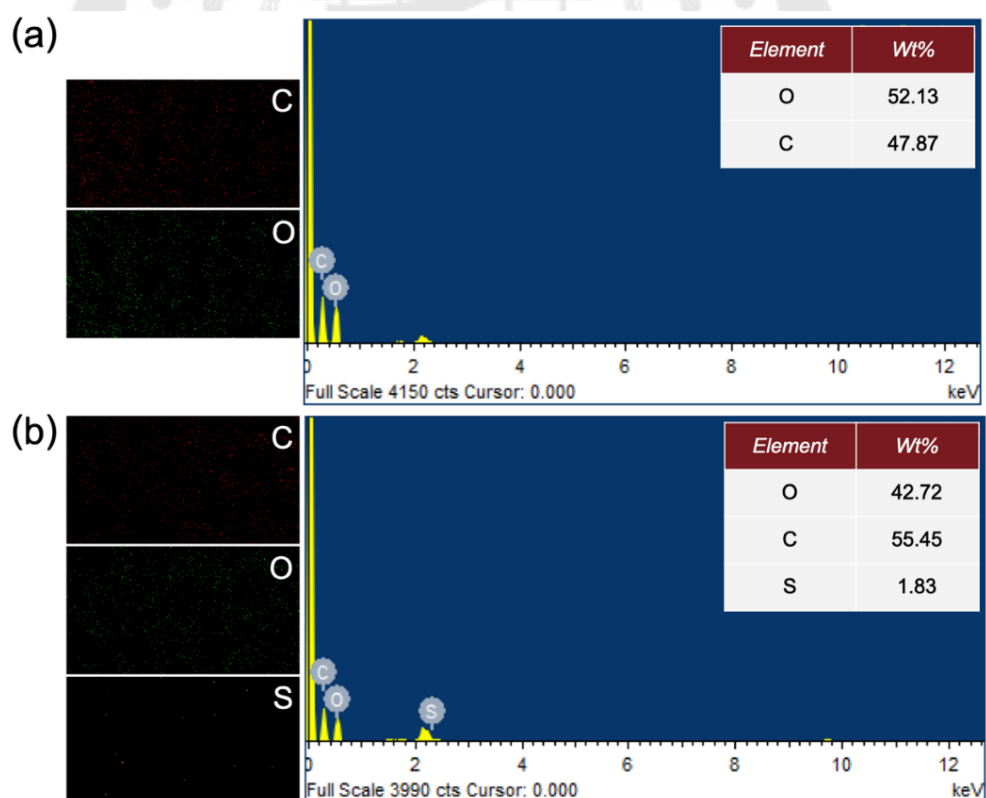


Figure 57 The EDS analysis and mapping results of each element of (a) pristine Rayon fabric and (b) Rayon/P3HT 150 mg.

#### 4.1.2.2 Chemical structure characterization of Rayon fabric and Rayon/P3HT composite fabrics

After studying the surface morphology of Rayon and Rayon/P3HT fabrics, the chemical structure's characterization is also essential to support the success of the composite fabric between Rayon fabric and P3HT powder. ATR-IR and Raman spectroscopy are then used for functional group and chemical bonding identification. The ATR-IR spectra were collected within a range of  $3000\text{--}700\text{ cm}^{-1}$ . According to Figure 58a, the Rayon fabric (Red line) demonstrates the characteristic peaks of Rayon molecular structure. The peak at  $2894\text{ cm}^{-1}$  corresponds to a stretching vibration of C-H group. Those peaks at  $1641\text{ cm}^{-1}$  and  $1366\text{ cm}^{-1}$  attribute to bending vibration of H-O-H and  $\text{CH}_2$  groups (68). The peaks observed at  $1019\text{ cm}^{-1}$  and  $890\text{ cm}^{-1}$  represent the stretching vibration of C-O-C group and OH-group, confirming the regenerate cellulose molecule (69). The wavenumber of each characteristic bond of Rayon is listed in Table 5. All the conditions of Rayon/P3HT composites show the ATR-IR peaks, which is similar to the characteristic peaks of Rayon fabric. Due to a small amount of P3HT content to Rayon fabric, the Rayon fabric cover over the peaks of P3HT characteristic. So, the molecular vibration of P3HT molecule could not be observed.

Raman spectroscopy, another suitable technique, was used to support the ATR-IR results for confirming the completely coated of P3HT on the Rayon fabric, which enables the details insight the polarizability caused by molecular structure vibration. The Raman result is shown in Figure 58b within a region of  $500\text{--}3500\text{ cm}^{-1}$  of Raman shift. The presence peaks of Rayon fabric were identified in Table 6. The Rayon fabric illustrates the Raman peaks at  $2900$  and  $1412\text{ cm}^{-1}$  attributing to the stretching vibration and bending vibration of  $-\text{CH}_2$  bonds, where the peak at  $1116\text{ cm}^{-1}$  presents a strong stretching vibration of C-C bond. All of the observed Raman peaks that corresponding to the molecular structure of Rayon fabric that also corresponds to the reported work by R. Khwanming, et., al., (70) and L. Ling Cho, et., al. (68). Notably, the characteristic

peaks of P3HT molecule can be evidently observed for all conditions of Rayon/P3HT composite fabrics. The Raman peaks at  $760\text{ cm}^{-1}$ ,  $1330\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$  of the C-S-C stretching, C-C intra-ring stretching and symmetric C=C correlating with the quinoid ring of P3HT (62,63) can be clearly identify. Meanwhile, the peak of  $\text{-CH}_2$  stretching vibration from Rayon is still shown. The containing of both Rayon and P3HT characteristic peaks can confirm that the Rayon fabric is completely composited with P3HT powder.



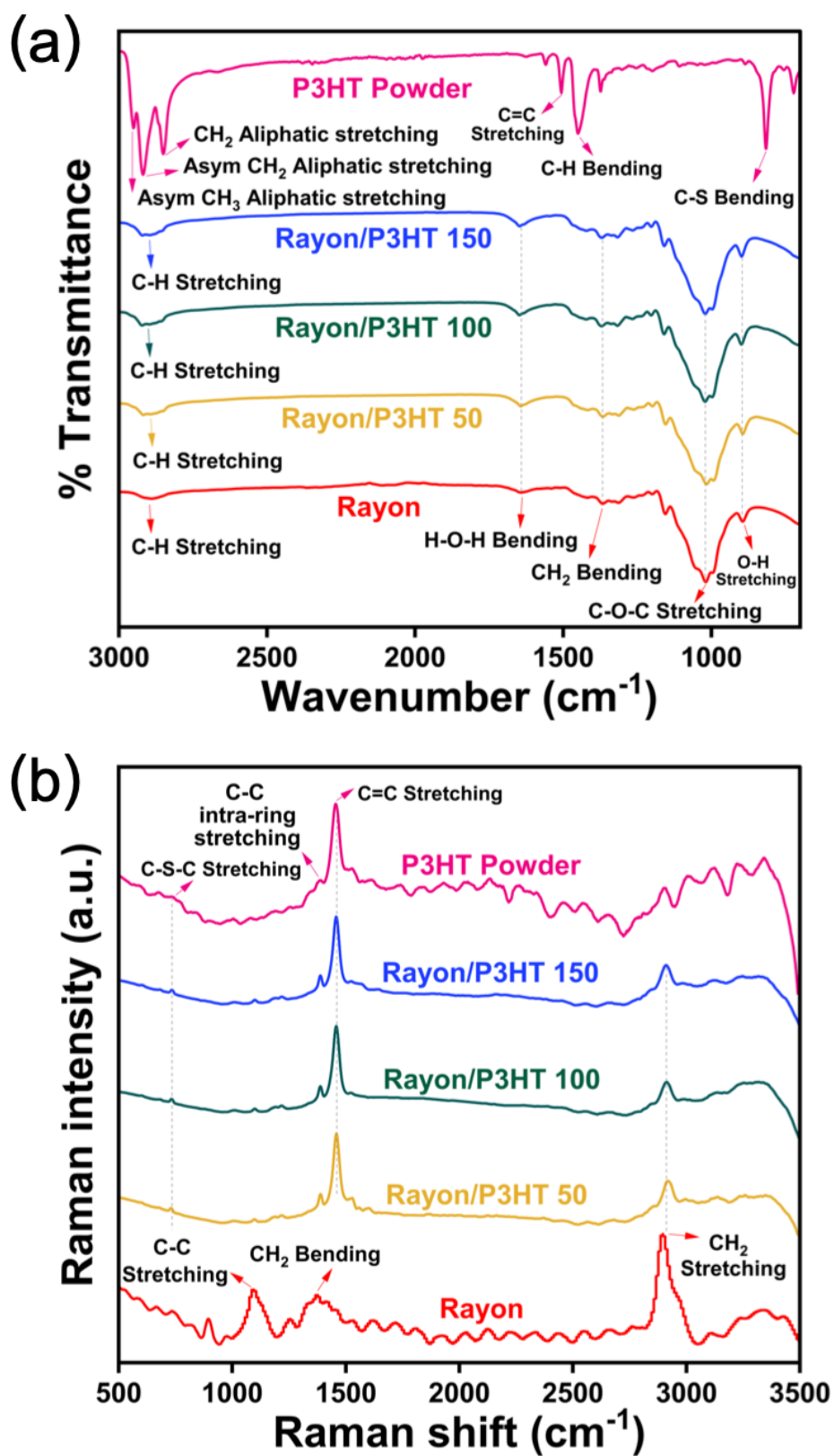


Table 5 The ATR-IR peaks identification list of Rayon fabric

| Wavenumber ( $\text{cm}^{-1}$ ) | Characteristic bond   |
|---------------------------------|-----------------------|
| 2894 $\text{cm}^{-1}$           | C-H stretching        |
| 1641 $\text{cm}^{-1}$           | H-O-H bending         |
| 1366 $\text{cm}^{-1}$           | $\text{CH}_2$ bending |
| 1019 $\text{cm}^{-1}$           | C-O-C stretching      |
| 890 $\text{cm}^{-1}$            | O-H stretching        |

Table 6 The Raman spectra identification list of Rayon fabric

| Raman shift ( $\text{cm}^{-1}$ ) | Characteristic bond      |
|----------------------------------|--------------------------|
| 1116 $\text{cm}^{-1}$            | C-C stretching           |
| 1412 $\text{cm}^{-1}$            | $\text{CH}_2$ bending    |
| 2900 $\text{cm}^{-1}$            | $\text{CH}_2$ stretching |

After the characterization of P3HT powder, Rayon fabric and Rayon/P3HT composite fabrics were scientifically discussed, the composite between the P3HT powder and Rayon fabric was confirmed. Furthermore, to explain the hybrid TENG-TEG based on Rayon/P3HT, the electrical and thermoelectric properties with the output efficiency are the important factors to evidence and test the performance of the hybrid TENG-TEG system.

#### 4.1.3 The electrical properties, thermoelectric properties and output efficiency of Rayon fabrics and Rayon/P3HT composite fabrics

The electrical properties and thermoelectric properties of Rayon and Rayon/P3HT fabrics were investigated by LCR meter and handheld digital multimeter (DMM). The scientific discussion of thermoelectric and electrical properties consists of Seebeck coefficient ( $S$ ), power factor ( $PF$ ), impedance analysis, conductivity and resistivity. For the electrical output performance in terms of the open-circuit voltage

( $V_{oc}$ ), short-circuit current ( $I_{sc}$ ) and maximum output power ( $P_{max}$ ), the signal data was collected by using an oscilloscope and a digital multimeter (DMM). In addition, the working mechanism of hybrid device was explained in this part to support the electrical output results.

#### 4.1.3.1 The electrical properties of Rayon fabrics and Rayon/P3HT composite fabrics

First, the impedance ( $Z$ ) was measured by LCR meter with various frequencies between 100 to 15 MHz within 300 sec at fixed temperature of RT. The imaginary part of impedance ( $Z''$ ) and the real part of impedance ( $Z'$ ) as a function of P3HT contents was collected and its relation was plotted as shown in Figure 59. The impedance semi-circular loop of  $Z''$  and  $Z'$  is called Nyquist plot (71) that represents the resistivity of samples. The results demonstrate the difference of loop's diameter, corresponding to difference resistivity values. The resistivity was increased with an expanding of loop's diameter (72,73). However, the impedance of Rayon/P3HT system is not represented in form of semi-circular loop but performed in nearly vertical line with different diameter similar to a work reported by M. Yutaka. et.al (74). The Rayon fabric with no additional P3HT exhibits a longest diameter at higher frequency compared with other conditions. At low frequency, the impedance of Rayon/P3HT shows more linearity. The Rayon fabric (Red line) possesses the highest resistivity, followed by the Rayon/P3HT-50 mg (Yellow line) and Rayon/P3HT-100 mg (Green line), respectively. Meanwhile, the Rayon/P3HT-150 mg (Blue line) show the smallest. The results confirm that the resistance of Rayon/P3HT composite fabrics decreased with an extending of P3HT content. The maximum of P3HT at 150 mg evidence the lowest resistivity among all conditions. Moreover, the impedance of Rayon/P3HT-150 mg was measured at difference temperature as a function of various frequencies between  $10^2$ - $10^6$  Hz, as shown in Figure 60. It can be seen from the result that the presence of highest impedance value occurred at 1kHz and temperature of  $100^\circ\text{C}$ . Meanwhile, the condition at  $40^\circ\text{C}$  exhibits the lowest impedance value at 1kHz. The results can conclude that the decreasing of the  $Z'$  values not depend on the rising of temperature but relating to the

working temperature of P3HT conductive polymers (75). The P3HT has normal working temperature at 40-70°C. Hence, the use of Rayon/P3HT in the application of TENG-TEG device to create the 40°C of temperature by sliding contacting is possible.

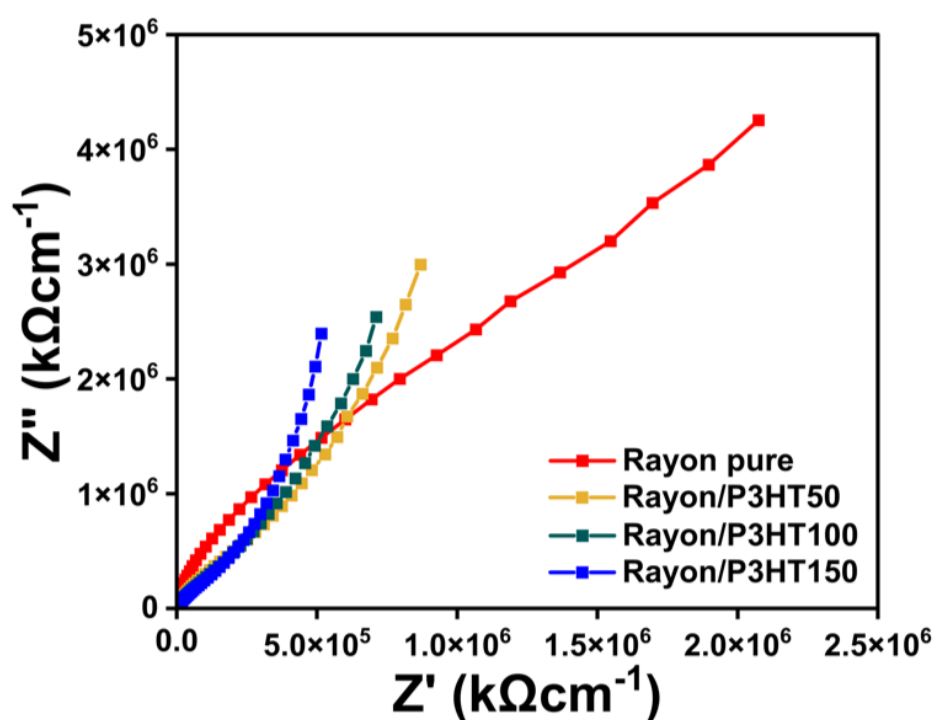


Figure 59 The Nyquist plots display the  $Z''$  and the  $Z'$  impedance of pristine Rayon and Rayon/P3HT fabrics for 50, 100 and 150 mg condition.

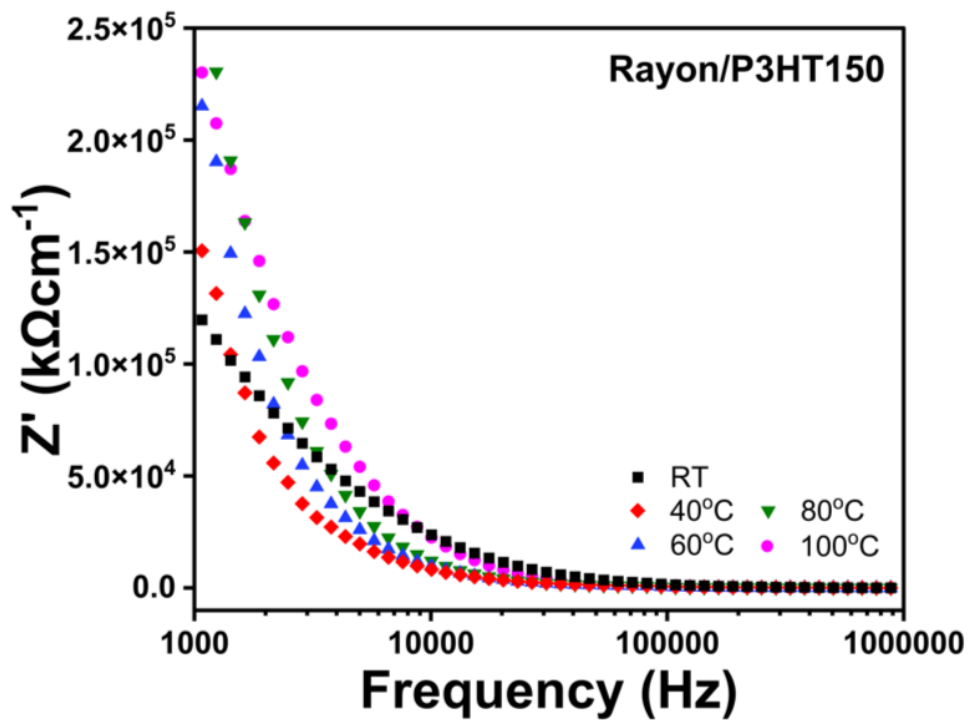


Figure 60 The impedance analysis illustrates the  $Z'$  impedance of Rayon/P3HT 150 mg as a function of temperature at various frequency from 1 kHz to 1 MHz

In addition, to support the resistivity of Rayon/P3HT fabrics, the electrical conductivity was also analyzed. In Figure 61, the conductivity as a function of frequencies (100, 1K, 10K and 100K Hz) at room temperature is presented. At low frequency of 100 Hz, the pristine Rayon fabric provides the lowest conductivity. Meanwhile, the frequency increased with a rising of conductivity. So, at highest frequency, the conductivity of pristine Rayon fabric was increased to  $1.7 \times 10^{-4}$  mS/cm. All of the Rayon/P3HT also behave in the same trend with an increasing of conductivity at 1,000, 10,000 and 100,000 Hz in order, comparing to pristine Rayon fabric. Moreover, as the P3HT content rises, the conductivity is also increased from 50, 100 and 150 mg conditions, respectively. Whereas the highest conductivity of  $3.5 \times 10^{-4}$  mS/cm was given by Rayon/P3HT-150 mg at highest frequency of 100kHz, which is 2 times greater than that of pristine Rayon fabric. Therefore, it can be concluded that an additional P3HT filler can significantly improve the conductivity of the pristine Rayon.

Furthermore, the conductivity of Rayon/P3HT-150 mg as a function of frequency at difference temperature between RT to 100°C was measured, and the results are illustrated in Figure 61. The reported conductivity of Rayon/P3HT-150 mg is in the same trend for all frequency ranges. As shown in Figure 62, the lowest conductivity is reported at room temperature. Interestingly, the highest conductivity is observed at 40°C with an essential factor of working temperature at 40-70°C of P3HT (75). This result of electrical conductivity shows agree well with the impedance tendency as mentioned above that confirm the essential factor of additional P3HT. According to M. J. Panzer et.al. research, the effect of holes density on the conductance was studied. They reported that the large conductance of P3HT was obtained with a large density of holes carrier (76). So, at the largest amount of P3HT consisted in Rayon fabric, the highest charge carrier concentration of P3HT conductive polymers can be possibly created. This is the reason Rayon/P3HT-150 mg enhances the best electrical efficiency compared to another amount of P3HT.

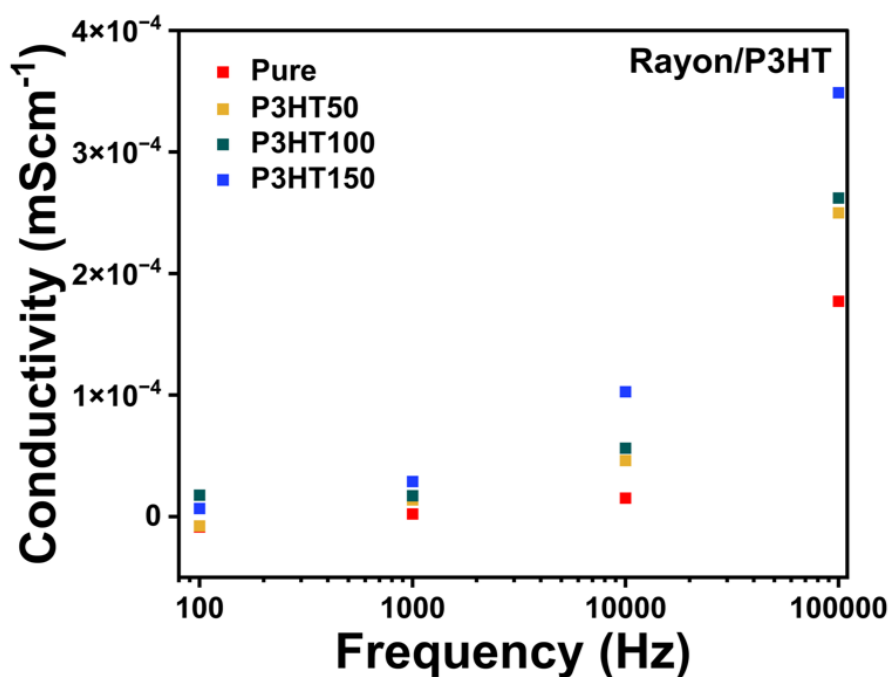


Figure 61 The electrical conductivity analysis of pristine Rayon and Rayon/P3HT fabrics for 50, 100 and 150 mg conditions.

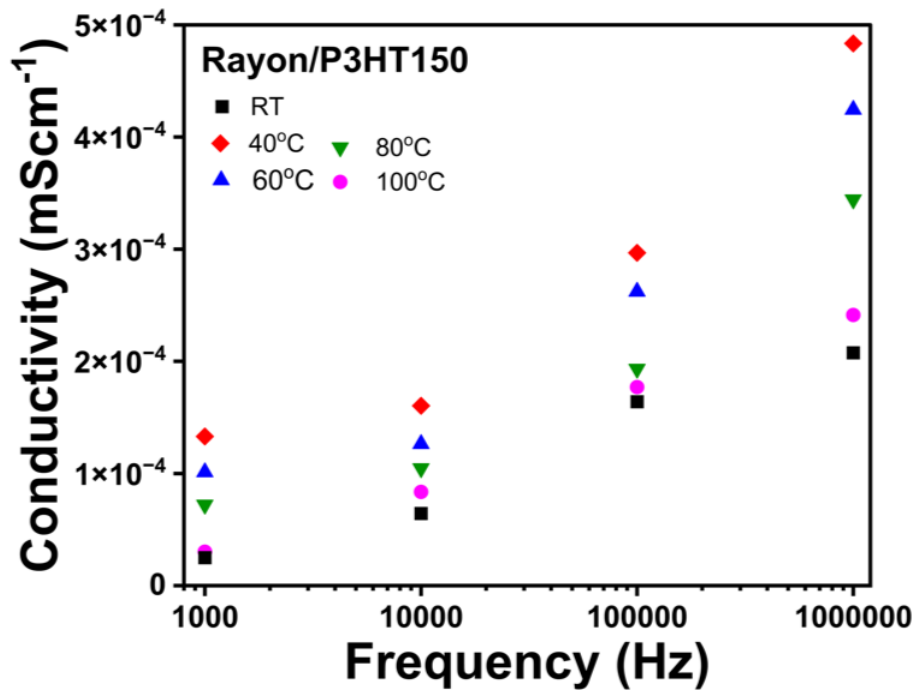


Figure 62 The electrical conductivity analysis of Rayon/P3HT-150 mg as a function of temperature at various frequency form 1 kHz to 1 MHz

#### 4.1.3.2 The thermoelectric properties of Rayon fabrics and Rayon/P3HT composite fabrics

Other than the electrical properties, thermoelectric properties are an important factor for hybrid TENG-TEG to confirm the thermoelectric in the system. According to the thermoelectric mechanism, the Seebeck effect needs to be mentioned for the determination of electricity generation with heat. To examine the Seebeck coefficient ( $S$ ) of materials, it is essential to permit the conversion of thermal energy to electricity. The coefficient can be used relating to Equation 1 ( $S = \frac{\Delta V}{\Delta T}$ ) by measure the gradient of voltage ( $\Delta V$ ) with the responding of temperature gradient ( $\Delta T$ ). The  $\Delta V$  comes from the different between voltage at hot side ( $V_{hot}$ ) and cold side ( $V_{cold}$ ). Meanwhile, the  $\Delta T$  comes from the different temperature between hot side ( $T_{hot}$ ) and cold side ( $T_{cold}$ ) (55). The measurement was set up by simple laboratory-experiment at initial temperature of RT, following Zhang and co-worker procedure (77). The

preparation of the samples starts by attaching the electrodes of aluminum tape to both end sides of the cut-Rayon fabric and Rayon/P3HT for all conditions (50, 100 and 150 mg). One side of all samples were plated on the laboratory hot-plate and heat up to 40°C to act as  $T_{hot}$ . While the other side of the samples are on the tray at  $T_{cold}$  of RT to simulate the TEG structure with  $\Delta T$  (78). According to the working mechanism of TEG, when the system reaches the  $\Delta T$ , the charges carriers from the heater side then move to the colder side which generates the thermo-voltage ( $\Delta V$ ). Subsequently, the  $V_{hot}$  and  $V_{cold}$  were measured by the hand-held digital multimeter, followed by calculated the  $S$  by Seebeck coefficient formula in Equation 1. The other important value of power factor ( $PF$ ) was also studied. The calculation of  $PF$  was quantified to assess the thermoelectric performance, by Equation 4. Where  $\sigma$  is the electrical conductivity of materials (55).

$$PF = S^2 \sigma$$

Equation 4. The thermoelectric power factor formula

The result of  $S$  and  $PF$  was plotted together and shown in Figure 63. The calculated  $S$  presents the positive values which can confirm the behavior of p-type thermoelectric materials for P3HT (79). The pristine Rayon fabric shows the lowest  $S$  values of 7.8 mV/K. Then, at the same gradient of temperature, the  $S$  increased with an increase of adding P3HT content. By adding P3HT of 150 mg, the  $S$  can be increased from 7.8 to maximum 16.3 mV/K. It clearly shows that the Rayon/P3HT 150 mg exhibits a higher  $S$  value than that of the pristine Rayon fabric for 2 times. The reason is that the charge carriers is increased with the additional P3HT (80) after temperature gradient is made by heating. The calculated  $S$  can be used to confirm the effect of thermoelectric property of the Rayon/P3HT system.

As illustrated in Figure 63, the  $PF$  of Rayon/P3HT demonstrates in relation to  $S$  value as a function of P3HT content. The  $PF$  results show the same trend as  $S$ , relating to the additional P3HT content that was increased by increasing of P3HT from 50-150 mg.

The maximum  $PF$  value of 0.7 W/mK was provided by Rayon/P3HT-150 mg which is the largest amount of the composite. It can conclude that the additional P3HT affects both  $S$  and  $PF$  values.

Moreover, the  $PF$  of Rayon/P3HT at 150 mg condition as a function of temperature (RT-100°C) was studied. The  $PF$  results is demonstrated in Figure 64, which show the increase of  $PF$  value from RT to at 40°C that the maximum  $PF$  of 0.13 W/mK could be reached. At higher temperature than 40°C, the  $PF$  values are constantly fallen off and finally attained 0.06 W/mK at 100°C. The result of this  $PF$  is consistent well with the result of impedance and electrical conductivity that achieve the highest performance at 40°C. Therefore, it can be also concluded that an increasing of  $PF$  value also not depends on the expanding of temperature, but relative to the working temperature of P3HT conductive polymers (75). According to the literature, M. Bharti *et al.* also reported the temperature dependence of  $S$  and  $PF$  (75) that the highest  $S$  and  $PF$  values was also found at 40°C in that case.

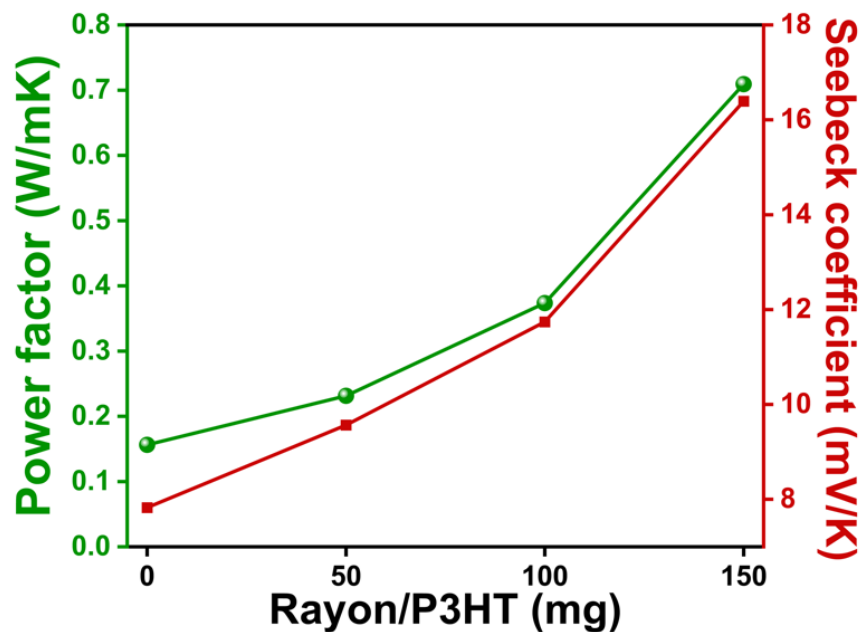


Figure 63 The Seebeck coefficient as a function of P3HT content (0, 50, 100 and 150 mg) in relation with calculated thermoelectric power factor value

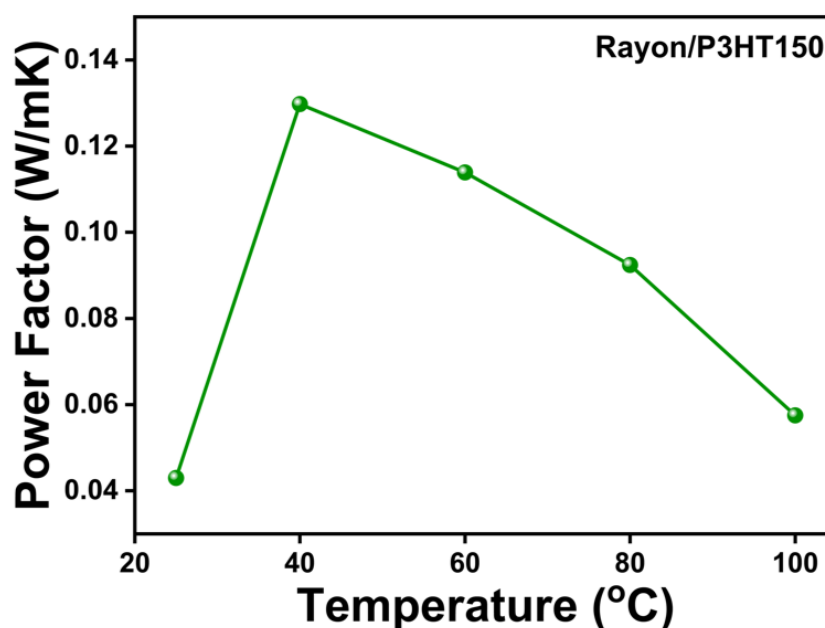


Figure 64 The calculated power factor of Rayon/P3HT-150 mg as a function of temperature (RT-100°C).

However, the conductive polymers are separated into two types, consisting of p-type and n-type thermoelectric materials. According to the study, the P3HT was classified in p-type conductive materials (38). Similar to semiconductor materials, the *J-V* curves were characterized to confirm the p-n junction effect of thermoelectric Rayon/P3HT composite. Starting with samples preparation, all the samples consisting of p-type and n-type materials were prepared to characterize the *J-V* curves by LCR meter. The Rayon/P3HT composite fabrics act as p-type thermoelectric materials, whereas the n-type thermoelectric material was studied. The flexible n-type thermoelectric material was reported in Yufei. Ding. et.al. work. They reported the high performance of silver selenide ( $\text{Ag}_2\text{Se}$ ) film on nylon film membrane (81). Also, the work of M. Daiva et.al. presented the  $\text{Ag}_2\text{Se}$  on polyamide fabric was successfully prepared (82). So,  $\text{Ag}_2\text{Se}$  powder was selected to coat with Rayon fabric for acting as n-type materials in this work. Each p-type and n-type material was spliced together and

connected with an electrode at both sides. The schematic diagram of sample structure is shown in the inset image of Figure 65. The  $J$ - $V$  curve was plotted to exhibit the relationship of current density and voltage as a function of various amount of P3HT (0, 50, 100 and 150 mg). Usually, the  $J$ - $V$  curves were behaved in S-curve form to present the p-n junction effect, consisting of zero bias, forward bias and backward bias (83). In this work, the voltage was biased between -5 to 35 V aiming to achieve the characteristic  $J$ - $V$  curves. The positive voltage represents the forward region. So, in this system the curves only represent in semi-linear line of forward bias, showing the region of increase biased voltage relation to the increasing of current density. According to the other work, the  $J$ - $V$  curves of P3HT front cell in a work of Danila S. et.al. (84) exhibit both linear and nearly linear lines which present a same behavior in Rayon/P3HT system. However, the current density of Rayon/P3HT shows a higher in values. Therefore, the Rayon/P3HT-150 mg obviously shows the best performance which confirms the p-n junction of thermoelectric property of Rayon/P3HT system. All of the thermoelectric results evident the thermoelectric mechanism of the hybrid TENG-TEG system.

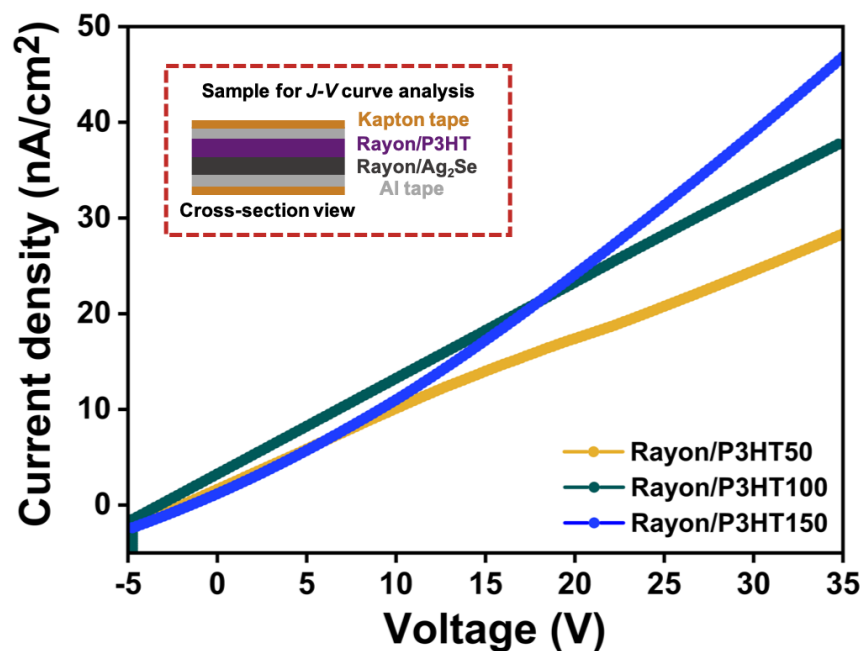


Figure 65 Characteristic  $J$ - $V$  curves of Rayon/P3HT at 50, 100 and 150 mg conditions

#### 4.1.3.3 The working mechanism and electrical output performance of Rayon fabrics and Rayon/P3HT composite fabric hybrid TENG-TEG devices

The electrical output performance of pristine Rayon and Rayon/P3HT composite fabrics was collected by using an oscilloscope and a DMM. The discussion focused on  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  of Rayon/P3HT and hybrid TENG-TEG device. In addition, the working mechanism of hybrid device was explained in this section firstly to support the electrical output results.

##### 4.1.3.3.1 The electrical working mechanism of Rayon/P3HT composite fabric hybrid TENG-TEG device

According to the working mechanism of Rayon/P3HT hybrid TENG-TEG device, the structure of the device was simulated along with the discussion. The hybrid TENG-TEG device was represented in the lateral-sliding mode (LS-mode), consisting of two different tribo-materials or known as contact layers. The Rayon/P3HT fabric basically acts as tribo-positive material due to electron donating ability of Rayon (70) and p-type thermoelectric materials of P3HT which contain holes carrier or positively charges (85). Whereas Teflon is tribo-negative materials owing to electron acceptor ability. The two layers were placed in parallel direction and attached with each electrode of conductive fabric (CD fabric) and aluminum tape (Al tape). The simulation image of the Rayon/P3HT hybrid TENG-TEG device structure within LS-mode working mechanism is represented in Figure 66. In the beginning, the full contact of two triboelectric layers occurs initially, creating the difference charges on each surface of layer. At this state, the charges are equal on both sides because there is no charge transfer occurrence to the external load. Therefore, the current is not created at this stage. Subsequently, the sliding outward motion is started by the upper layer (Rayon/P3HT fabric) transpose in parallel until reaching the full motion along the fixed bottom layer (Teflon film), as shown in state I-II. The imbalanced triboelectric charges on Rayon/P3HT and Teflon induced opposite charges to occur at electrodes on each side. The positively charges created on Al bottom electrode transfers up to the CD fabric (top electrode), resulting in the negatively charges. It reveals a potential difference with the flowing of output current in positive electrical signal. After that, the movement of the

upper layer continuously sliding inward with a connection of a few area still appeared, as shown in state III-IV (86). The charges of the top electrode then move backward to the bottom, generating the output to flow in the opposite direction which present in negatively output signal. According to the loop of mechanism, the alternating current (AC) waveform is turned out by repeating in sliding motion. Due to the hybrid TENG-TEG system, during the repletely sliding motion, the heat is then simultaneously created, leading the conductive polymers to produce more charges carrier from thermoelectric mechanism. Thus, the triboelectric charges on the surface are combined with charges carrier of conductive polymers illustrating capability to promote the higher electrical output within the combination between triboelectrification and thermoelectric effects.

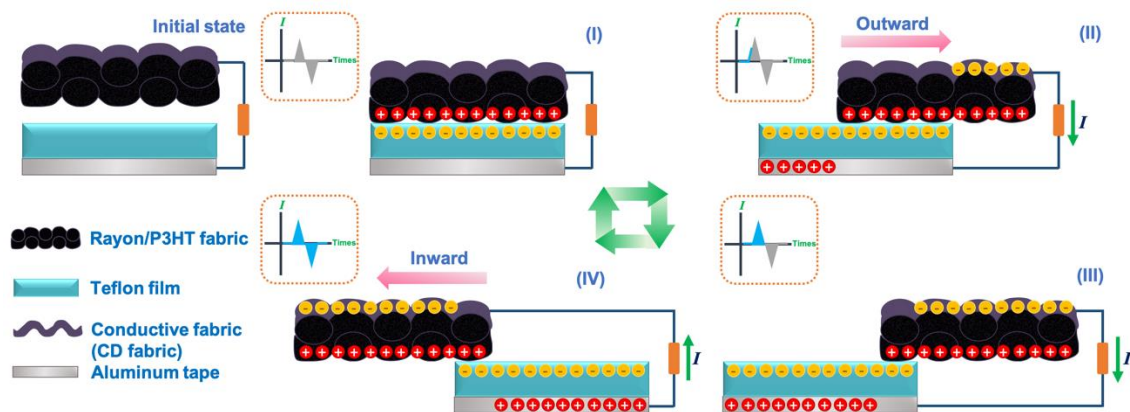


Figure 66 The working mechanism of Rayon/P3HT fabric hybrid TENG-TEG device within the lateral sliding mode.

#### 4.1.3.3.2 The electrical output of Rayon fabrics and Rayon/P3HT composite fabric TENG-TEG devices

In order to study whether the temperature is exactly one of the factors which affect the electrical output performance of the Rayon/P3HT hybrid TENG-TEG, the measuring of  $V_{oc}$  along with thermal camera capturing was simultaneously investigated. The voltage results are illustrated in Figure 67a with the thermal images in Figure 67b. The  $V_{oc}$  of Rayon/P3HT-150 mg condition was representatively measured by

sliding motion within 25 minutes. According to the  $V_{OC}$  plot in Figure 67a, the  $V_{OC}$  of hybrid TENG-TEG device was collected with the capturing thermal images every 5 minutes. It can be clearly seen from the results that the  $V_{OC}$  increased from 0 to ~47.3 V and reached maximum  $V_{OC}$  at ~53.3 V at 25 min. By matching  $V_{OC}$  results with color difference in thermal captured images, the rising of  $V_{OC}$  simultaneously occurred when the temperature was expanded. According to sliding motion mode, the heat source can also be generated as evidently shown in the heat zone of red area, as displayed in Figure 67b. The highest temperature in a range of 35-40°C was provided at heat zone within 25 minutes, which consistent with the working temperature of P3HT (75). Thus, one crucial factor that correlates to output efficiency is temperature.

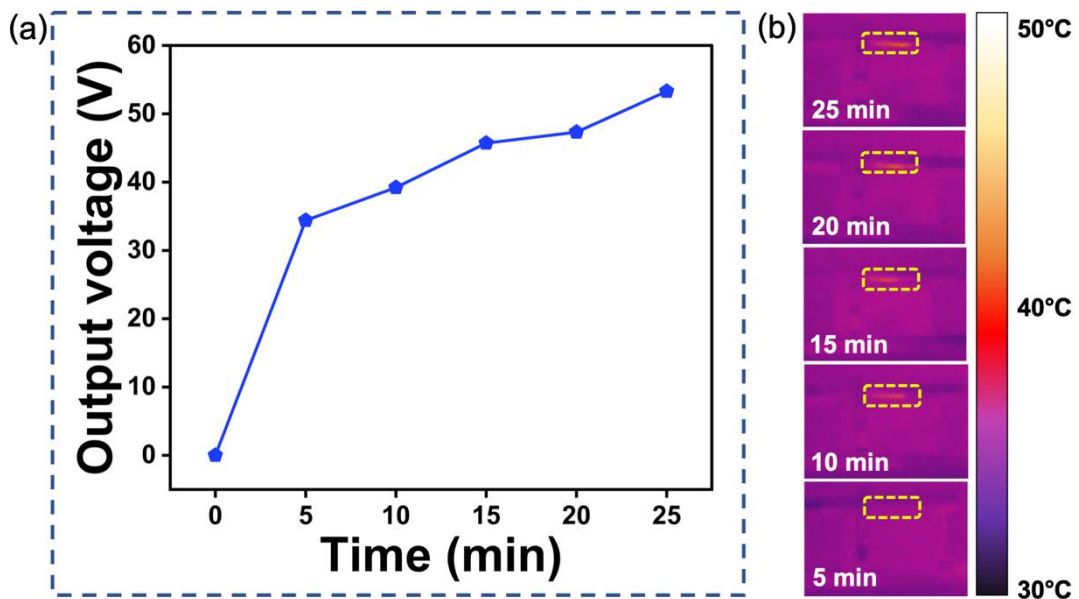


Figure 67 (a) The  $V_{OC}$  as a function of working times and (b) the thermal captured images of Rayon/P3HT fabric TENG-TEG device within sliding motion

After confirming the thermal rising factor relative to  $V_{OC}$  performance, the  $V_{OC}$  and  $I_{SC}$  of pristine Rayon fabric and Rayon/P3HT composite fabrics were investigated in two routes of unheated and heated systems. First, the  $V_{OC}$  and  $I_{SC}$

as a function of times were measured at room temperature (unheated system) within LS-mode mechanism are demonstrated in Figure 68a-b. The pristine Rayon fabric provides  $V_{oc}$  of about  $\sim 34.90$  V and  $I_{sc} \sim 16.0$   $\mu$ A which is the lowest value in this system. As compare with other research, a work of R. Khwanming, et., al. reported the output efficiency of pristine Rayon fabric within contact separation mode (70). They show the  $V_{oc}$  and  $I_{sc}$  of  $\sim 23.17$  V and  $\sim 13.08$   $\mu$ A which is nearby in values of Rayon fabric in this work, confirming the efficiency of pristine Rayon fabric. Both  $V_{oc}$  and  $I_{sc}$  of the Rayon could be clearly increased by compositing with P3HT conductive polymers. Along with the increasing of P3HT amounts to 50 and 100 mg, the  $V_{oc}$  of  $\sim 41.81$  V and  $\sim 45.78$  V was enhanced, whereas adding P3HT at the Rayon/P3HT-150 mg condition could reach the highest  $V_{oc}$  value of  $\sim 49.50$  V, as illustrated Figure 68a. The  $I_{sc}$  signal in Figure 68b exhibits in a same tendency of  $V_{oc}$ , which shows an increasing in  $I_{sc}$  from  $\sim 16.0$   $\mu$ A of pristine Rayon fabric to the larger  $I_{sc}$  values of Rayon/P3HT composite fabric. The Rayon/P3HT-50 mg and Rayon/P3HT-100 mg provided the  $I_{sc}$  of  $\sim 20.0$   $\mu$ A and  $\sim 30.0$   $\mu$ A. The highest  $I_{sc}$  of  $\sim 35.0$   $\mu$ A could be obtained by Rayon/P3HT-150 mg. The results clearly illustrate that the Rayon/P3HT-150 mg can generate higher performance of  $V_{oc}$  and  $I_{sc}$  than that of the pristine Rayon fabric by 1.4 and 2 times. It confirms the efficiency of adding P3HT in the Rayon. The scientific reason for the increasing of  $V_{oc}$  and  $I_{sc}$  goes to the increasing of charge carrier from P3HT after heat generating during mechanical sliding motion. According to the heat generation of continuously sliding motion, the P3HT conductive polymer could create the charges carrier which can combine with triboelectric charges of Rayon fabric to be able to export more charges to the external loads (29). So, both  $V_{oc}$  and  $I_{sc}$  increase with additional of P3HT amount, leading the Rayon/P3HT-150 mg to reach the highest output performance. However, the electrical output of Rayon/P3HT may probably increase when adding more than 150 mg of P3HT contents. By the limitation of commercial P3HT powders, the maximum amount of P3HT in this work is limited at 150 mg. The increasing of P3HT content relate to gain more

charge carriers concentration, while an excess of charges carrier combine with triboelectric charges are impractical to transfer out to the external load (87).

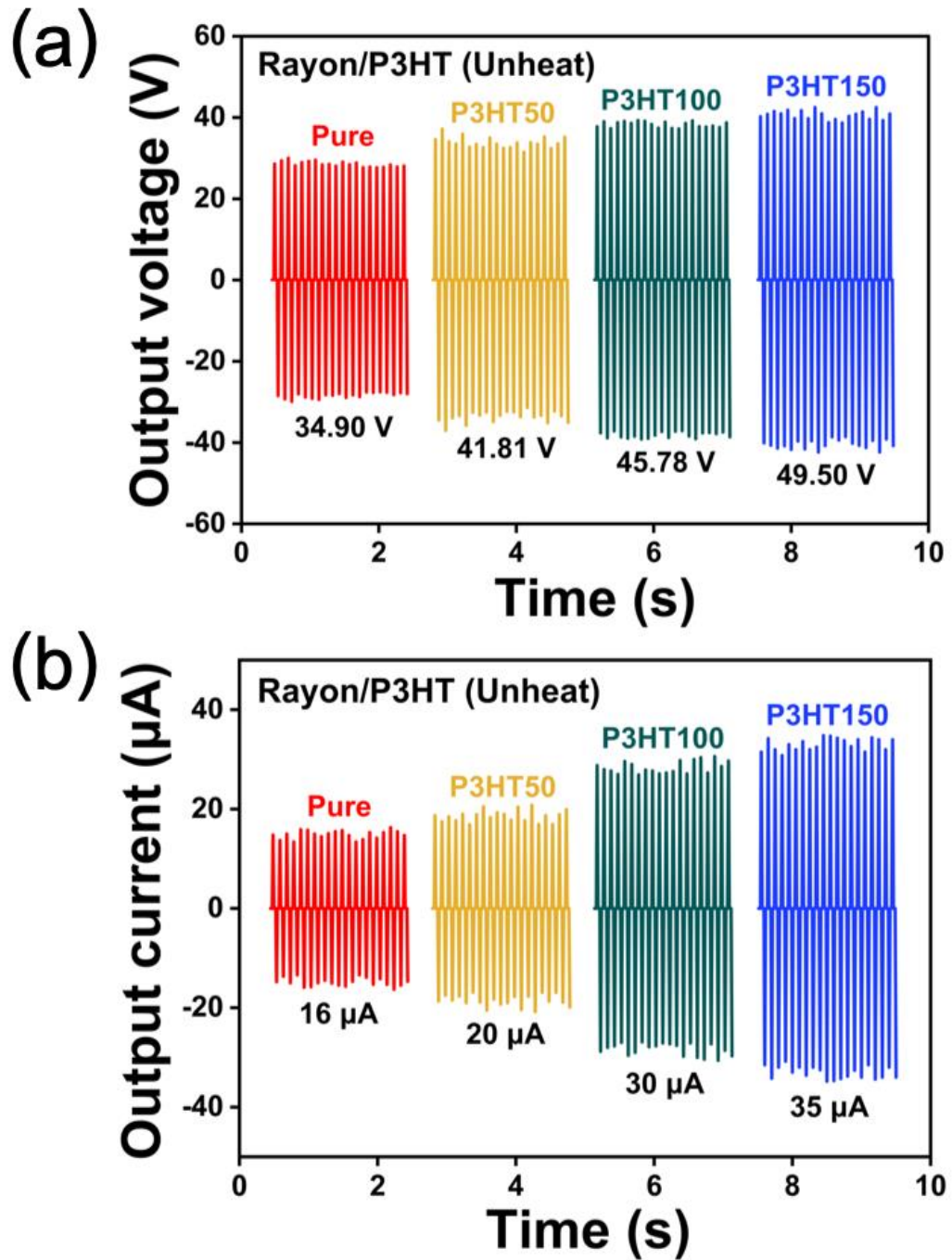
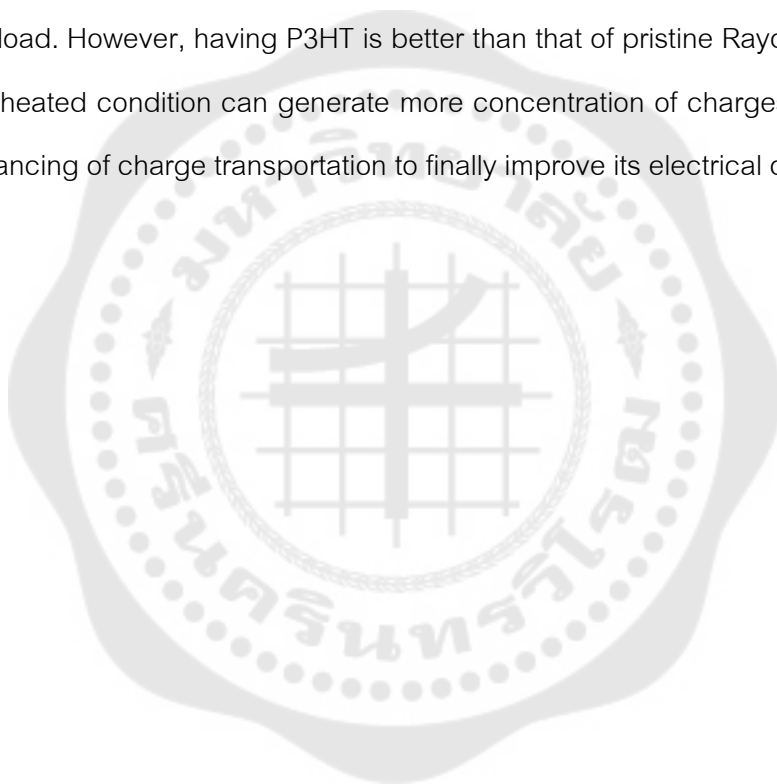


Figure 68 The electrical output performance in unheated system of (a)  $V_{oc}$  and (b)  $I_{sc}$  of Rayon/P3HT hybrid TENG-TEG device with varying P3HT amount

As mentioned in the part of electrical and thermoelectric properties, the working temperature of P3HT is in the 40-70°C period (75). The continue applying mechanical force from sliding motion at RT can only increase the temperature to 40°C. In order to survey the  $V_{OC}$  and  $I_{SC}$  at highest working temperature of 70°C, the heated system measurement was set by heating the Rayon/P3HT fabric at 70°C by ironing to support that the temperature is an essential factor of Rayon/P3HT hybrid device. According to Figure 68a-b, the  $V_{OC}$  and  $I_{SC}$  of pristine Rayon and Rayon/P3HT composite fabrics are represented. The pristine Rayon fabric generated the lowest in  $V_{OC}$  of ~42.01 V, followed by Rayon/P3HT-50 and 100 mg, which provided the  $V_{OC}$  of ~45.52 V and ~51.35 V, respectively. Whilst the Rayon/P3HT-150 mg could generate ~62.96 V which is the highest  $V_{OC}$  value in this case, as reported in Figure 69a. The  $I_{SC}$  results in Figure 69b is shown in the similar trend to the  $V_{OC}$ . Pristine Rayon gave the  $I_{SC}$  of ~20  $\mu$ A while the Rayon/P3HT-50 mg and 100 mg could enhance about ~39  $\mu$ A and ~42  $\mu$ A. The highest value of ~45.0  $\mu$ A could be generated by the Rayon/P3HT-150 mg that is 2.2 times higher than pristine Rayon fabric.

The results of heated condition demonstrate the same tendency with unheated system where both  $V_{OC}$  and  $I_{SC}$  rise correlate with an adding larger amount of P3HT. The reason is same as discussed above, the creation of charges by P3HT can combine with triboelectric charges on the surface to be able to export more charges to the external loads (29). The comparison between the Rayon and Rayon/P3HT output performance within heated and unheated condition is exhibited in Figure 70-71. By comparing the  $V_{OC}$  and  $I_{SC}$  between heated and unheated Rayon (Figure 70a-b), the output of  $V_{OC}$  and  $I_{SC}$  was increased by 1.2 times. Meanwhile, the  $V_{OC}$  and  $I_{SC}$  of Rayon/P3HT composite under heated condition was 1.3 times higher than that of unheated system at the same concentration of P3HT, as depicted in Figure 71a-b. It can be pointed out that the heat plays a crucial role in improving electrical output,  $V_{OC}$  and  $I_{SC}$ , for all conditions. Nevertheless, since the electrical output could be increased by heat in both case of

Rayon and Rayon/P3HT's systems, therefore, it cannot be clearly proved that this situation comes from only the thermoelectric behavior of P3HT. The possible reason for increasing electrical output can be probably explained by the combination of the two effects. First, the P3HT generates more mobile charges to the systems by its p-type behavior. The charges density is therefore enhanced. Second, the increasing output happens in both cases (Rayon and Rayon/P3HT) because thermal energy by heating can be a driving force to let the charge carriers move easily at the same time to the external load. However, having P3HT is better than that of pristine Rayon. The additional P3HT at heated condition can generate more concentration of charges carrier together with enhancing of charge transportation to finally improve its electrical output efficiency.



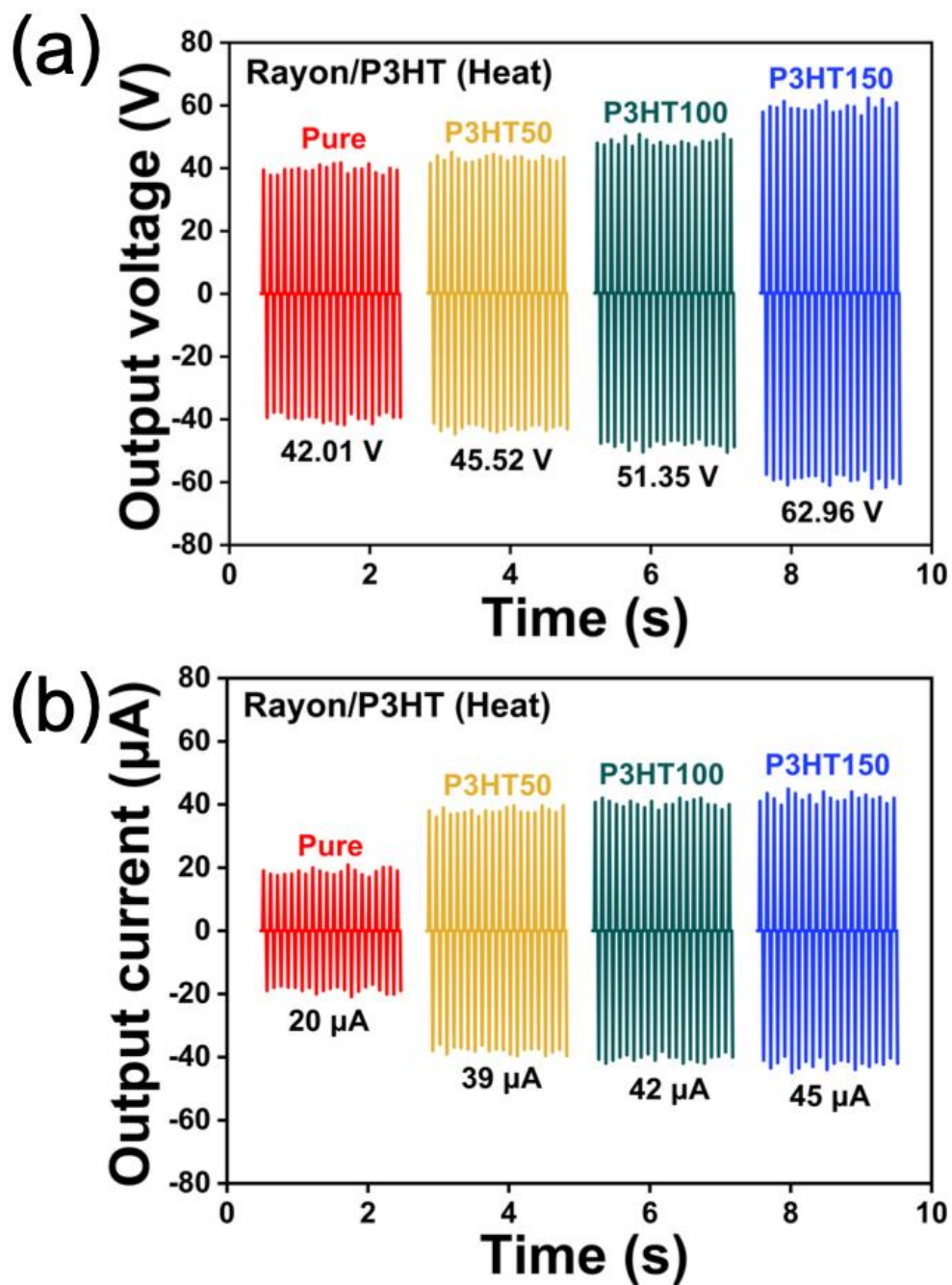


Figure 69 The electrical output performance within heated system of (a)  $V_{oc}$  and (b)  $I_{sc}$  for the Rayon/P3HT hybrid TENG-TEG device with various amounts of P3HT.

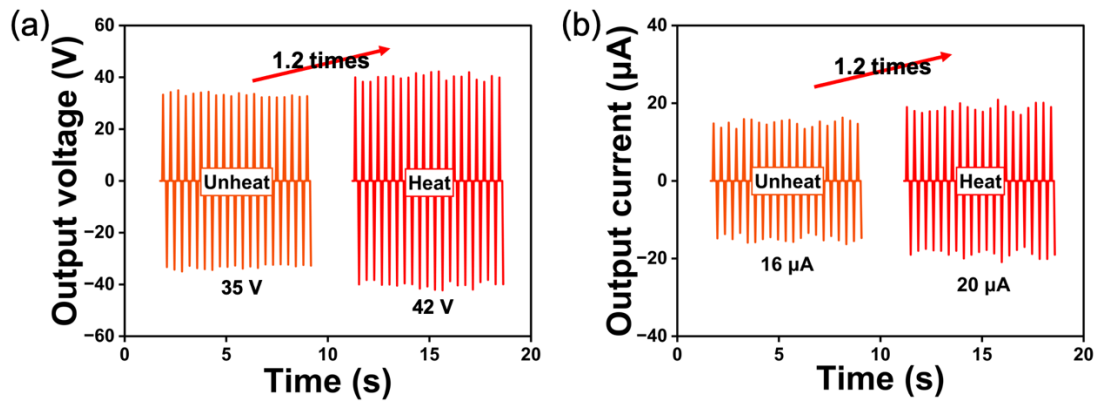


Figure 70 The comparison in terms of (a)  $V_{oc}$  and (b)  $I_{sc}$  within unheated and heated system of Rayon fabric

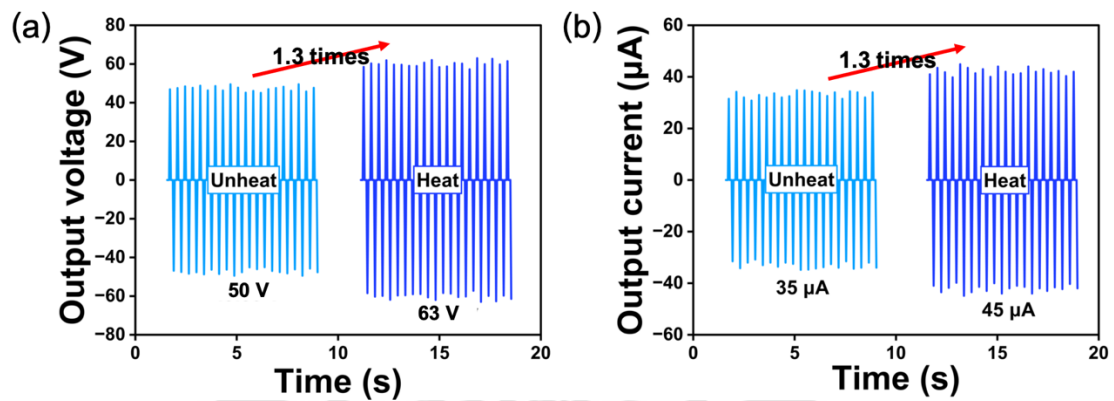


Figure 71 The comparison in terms of (a)  $V_{oc}$  and (b)  $I_{sc}$  within unheated and heated system of Rayon/P3HT hybrid TENG-TEG device at 150 mg of P3HT content

Before using with practical application,  $P_{max}$  of pristine Rayon fabric and Rayon/P3HT composite fabric was examined by connecting the device with the electrical circuit of bridge diode that contained the external load resistance before connecting to the oscilloscope. The resistance was varied in a range of  $1\text{k}\Omega$  -  $10\text{M}\Omega$  to obtain the effective output power of each material. The results demonstrate the relationship between output voltage and output current with the external resistance. The output voltage was achieved using an oscilloscope. Then, the output current was

calculated using Ohm's law ( $V=IR$ ). It can be seen from Figure 72a-b that the output voltage is clearly increased while the output current is decreased at higher load resistance corresponding to Ohm's law (88). Subsequently, the output power was calculated with a power formula ( $P=IV$ ) (89). The results of output power of pristine Rayon and Rayon/P3HT-150 mg as a function of load resistance are also displayed in Figure 71a and b, as indicated with blue line. To reach the maximum output power, the external and internal resistance needs to be matched together. The results of  $P_{max}$  is therefore found at specific value of load resistance. In Figure 72a, the  $P_{max}$  of pristine Rayon fabric is revealed approximately  $\sim 114.5 \mu\text{W}$  at  $1\text{M}\Omega$ , whereas in Figure 72b, the Rayon/P3HT-150 mg illustrates a maximum value about  $\sim 1204.1 \mu\text{W}$  at the same resistance of  $1\text{M}\Omega$ . The Rayon/P3HT-150 mg could generate the  $P_{max}$  by 10.5 times larger than that of the pristine Rayon fabric. This result concludes that the maximum condition of Rayon/P3HT-150 mg can enhance the highest output efficiency of  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  due to the promoting more charges carrier concentration as compared to other composite conditions in this system.

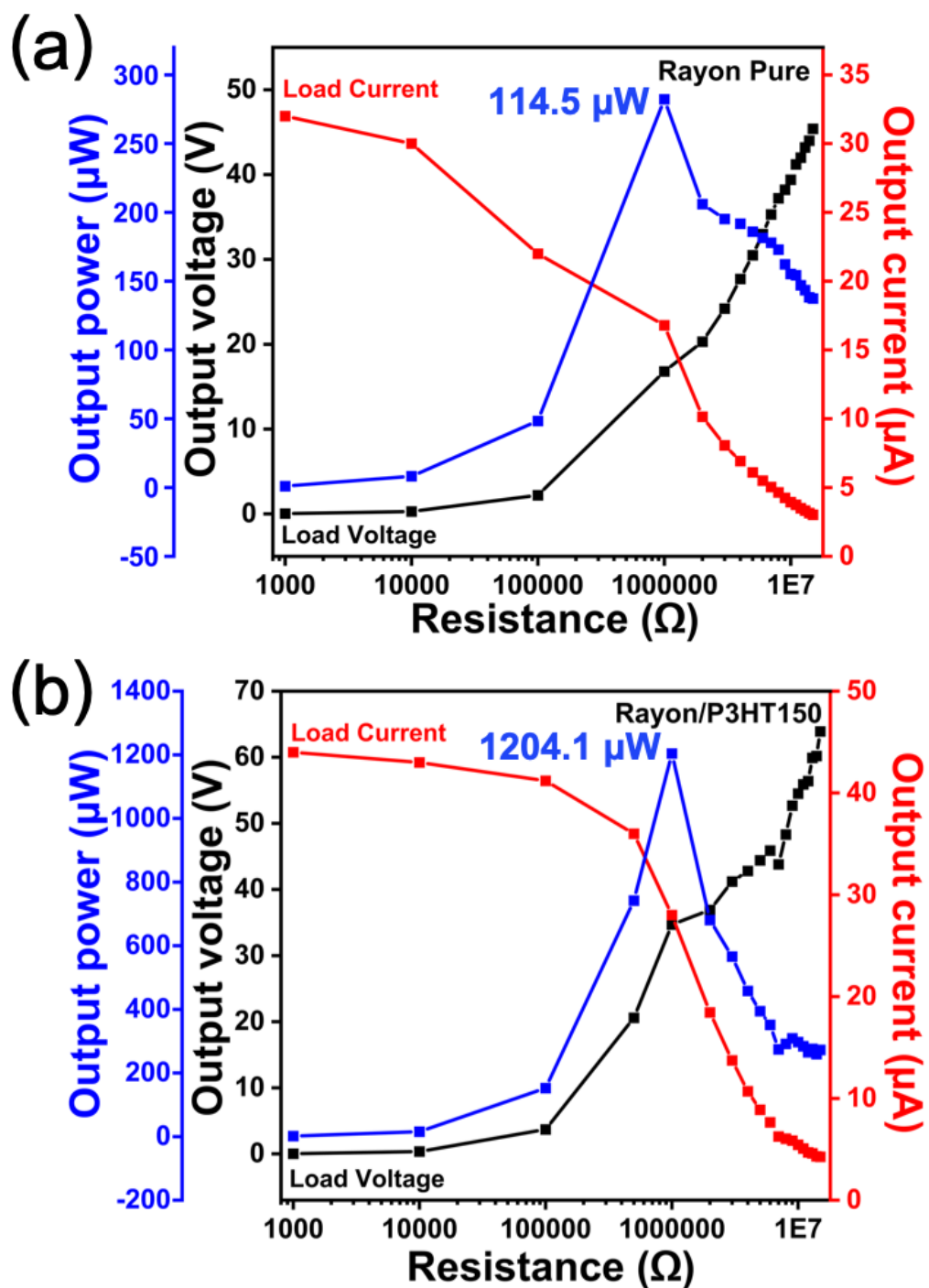


Figure 72 Output voltage, current and output power of (a) pristine Rayon fabric and (b) Rayon/P3HT-150 mg with various load resistance of 1kΩ - 10MΩ.

However, the study of other condition for P3HT composite systems in both Rayon/P3HT and Rayon/P3HTCNT was interrupted due to the two aspects of limitation. First, for the Rayon/P3HT/CNT system, the preparation of P3HT/CNT solution is

complicated and large amount of P3HT powder is required to composite with CNT. Also, because the completely mixed solution of P3HT/CNT is difficult to receive, the dip-coating of P3HT/CNT are then irregularly dispersed to Rayon fabric. The reason of this limitation is due to the smooth texture of Rayon fabric. Second, the cost of commercial P3HT powder is high and it takes long period at least four months of shipping. Combining these two reasons is too time consuming. Therefore, the study of higher condition for Rayon/P3HT, cotton/P3HT and the composite of cotton and Rayon fabrics with P3HT/CNT was decided to stop. The cellulose fabric/PANI and cellulose fabric/PANI/CNT was then studied instead for having a chance to fabricate high performance of hybrid TENG-TEG system.

#### **4.2 Cellulose-based fabric/PANI composite fabrics system**

According to cellulose-based fabric/PANI system, the fabric was separated into two kinds of Rayon and cotton fabric to composite with PANI and PANI/CNT as hybrid TENG-TEG. The detail of discussions in this section will be started with characterization of as-prepared PANI and PANI/CNT powder after polymerization and followed by fabric and fabric composite characterization. In the part of fabric and fabric composites, the experimental results will begin with the Rayon fabric system first, then follow by cotton fabric systems.

##### **4.2.1 Characterization of PANI and PANI/CNT powder**

In the part of PANI and PANI/CNT powder's characterization, the results of morphology performed by LOM and SEM are mentioned first. After that the phase identification and chemical structural characteristics from IR, Raman and XRD techniques will be discussed.

###### **4.2.1.1 Morphological characterization of PANI and PANI/CNT powder**

The digital images of PANI and PANI/CNT are illustrated in Figure 73a-b. The obtained PANI powder (Figure 73a) and PANI/CNT powder (Figure

73b) after polymerization shows the fine powder character with different colors. The PANI powder shows the dark green color while the PANI/CNT powder illustrates the black color due to the combination of CNT, as obviously see in each inset image of Figure 73a-b. It shows the same result with the Stoma. M. *et. al.* 's work which obtain a dark green powder of PANI and black color of PANI/CNT after synthesis by polymerization (90). Moreover, the surface morphology of PANI powder was observed by SEM as shown in Figure 74a-b. As can be seen in Figure 74a, the PANI powder shows branch-shape of secondary particles from compacted primary particle that are arranged together in network. An increase of magnification at 25000x in Figure 74b, leading to see a highly branched shape with small granular over the surface which similar to the morphology of PANI in another research of Andra, K. and *et. al.* that reported a highly branched nanofibrillar agglomeration (91). The SEM images of PANI/CNT powder show different morphology with PANI, as shown in Figure 74c. It shows semi-circular shape of PANI particles within a board size in micron range. The particles show an agglomeration which creates an irregular shape. An increase of the magnification at 25000x (Figure 74d) for SEM clearly illustrates a numerous tube of the CNT wrapping around the PANI particles. This CNT morphology could not be observed in PANI. The difference between PANI and PANI/CNT morphology is also report in Tanty N., and *et al.* (92). The results indicate that the PANI and PANI/CNT powder are synthesized.

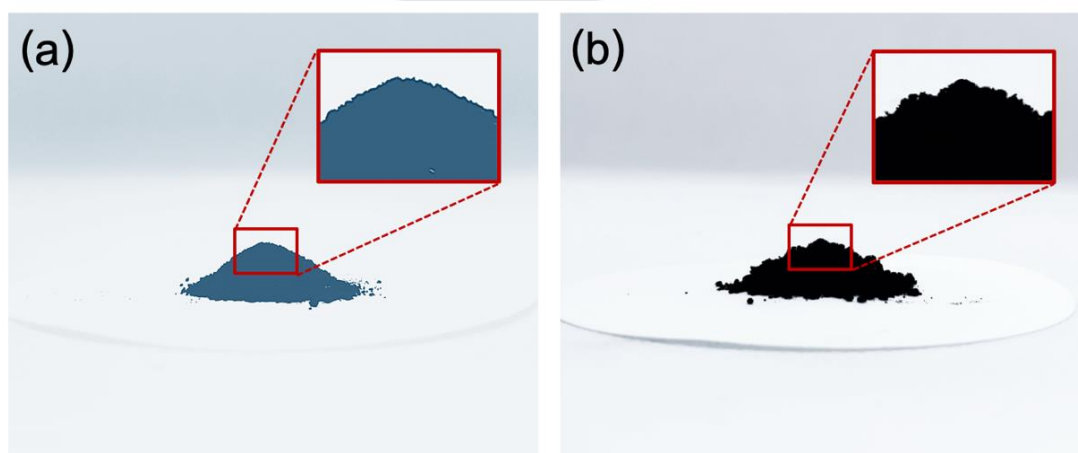


Figure 73 The digital images of (a) PANI and (b) PANI/CNT

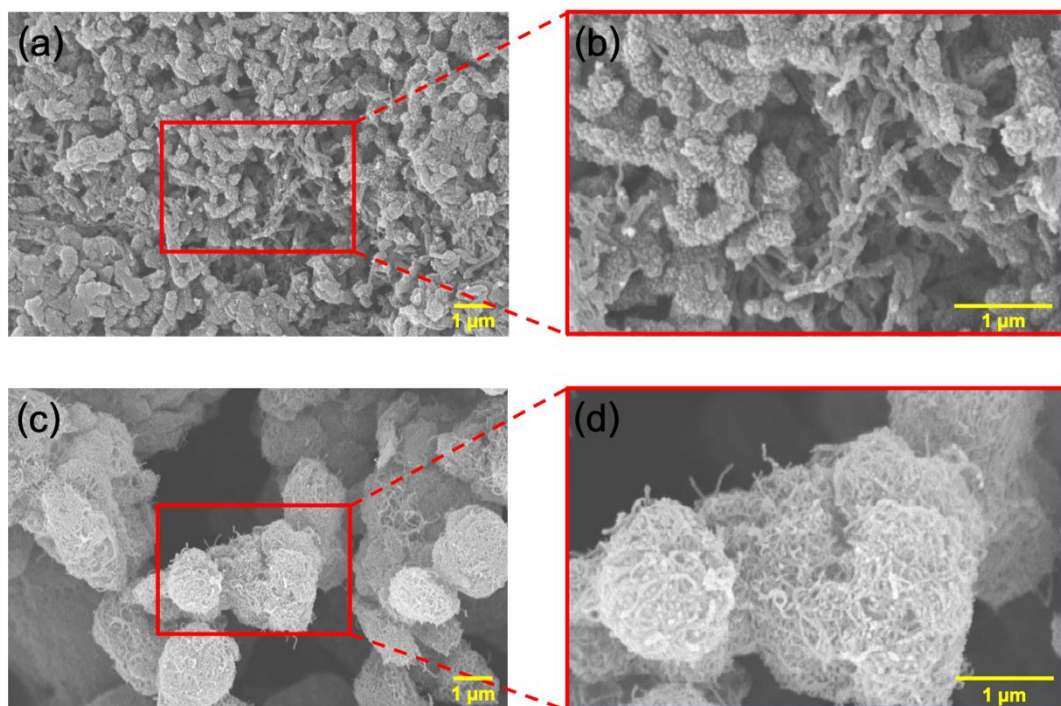


Figure 74 The SEM images of PANI powder with magnification of 10000x (a) and (b) 25000x, and SEM images of PANI/CNT powder at 10000x (c) and (d) 25000x.

#### 4.2.1.2 Chemical structure characterization of PANI and PANI/CNT powders

Functional groups and bonding in chemical structure of PANI and PANI/CNT were characterized by ATR-IR and Raman techniques. The ATR-IR results of PANI are compared with PANI/CNT to confirm the composite between two phases. The spectra are identified in the range of  $4000\text{--}500\text{ cm}^{-1}$ , as shown in Figure 75. The wavenumber of the IR peaks was summarized in Table 7. The evident peaks at  $\sim 3450$  and  $2925\text{ cm}^{-1}$  of PANI are corresponding to the stretching vibration of amine (N-H) group and C-H bonding with. The aromatic ring attached to the amine group is presented in three-small peaks at  $1598$ ,  $1465$  and  $1295\text{ cm}^{-1}$ . They attributed to the C=C stretching, C=N stretching and C-N stretching, respectively. Also, the peaks at  $1115$  and  $805\text{ cm}^{-1}$  are assigned the C-H bending vibration. All of the presence peaks above are corresponding to the characteristic PANI peak in the literature (93), showing the complete synthetic of PANI powder. Whereas, the peaks of PANI/CNT also illustrates the

stretching vibration of C=C, C=N and C-N group, which occurred from containing of an aromatic amine within PANI structure (94). Almost all the vibrational peaks that were observed in PANI/CNT are consistent with the spectra of the PANI, presenting the characteristic of PANI molecular structure. Notably, the ATR-IR results of PANI and PANI/CNT only show the presence of PANI characteristic peaks. Meanwhile the characteristic peaks of CNT still do not appear in this technique. The reason is due to consisting of C-C bond of CNT structure which usually a nonpolar bond, leading this bond to be inactive in IR technique (95,96).

To confirm the existence of CNT in PANI/CNT composite, the Raman technique was used and the Raman spectra of PANI and PANI/CNT is shown in Figure 76 within a region of 500-2500  $\text{cm}^{-1}$ . The results of both PANI and PANI/CNT illustrate the C-H stretching vibration at 1165  $\text{cm}^{-1}$  position that corresponds to the quinoid ring of PANI structure (92). The peaks at 1339  $\text{cm}^{-1}$  and 1486  $\text{cm}^{-1}$  are assigned to the C-N stretching and C=N stretching vibration. The two small peaks at 1556  $\text{cm}^{-1}$  and 1594  $\text{cm}^{-1}$  belong to the N-H bending and C=C stretching which represent the strong  $\pi$ -bonds in emeraldine form of PANI chemical structure. The observation of C-N and C=N stretching can also be seen in the report of Xia *et al.* (97), which show the Raman shift of PANI/CNT synthesized by chemical polymerization. The different Raman pattern for PANI/CNT powder as compared to the spectra of PANI powder was given to the CNT characteristic. The important peaks of CNT identification by D-band and G-band at 1346  $\text{cm}^{-1}$  and 1590  $\text{cm}^{-1}$  are presented. The D-band acts for the carbon structure defect (98) and the G-band represent the stretching vibration of  $\text{sp}^3$  hybridization of C atoms in CNT structure. On the contrary, the  $\text{sp}^2$  hybridization between C atoms in PANI structure are unable to observed both of D-band and G-band (99). Therefore, the Raman result can confirm that the PANI/CNT was successfully synthesized in this work.

The XRD patterns of PANI powder compared with PANI/CNT powder are shown in Figure 77. The peaks at  $2\theta$  around  $14.9^\circ$ ,  $20.6^\circ$  and  $25.4^\circ$  belong to (121), (113), and (322) crystal planes, which demonstrate the part of crystalline in the semi-crystalline PANI structure (98). Meanwhile, the XRD peaks showing CNT characteristics was

observed in PANI/CNT sample at  $2\theta$  of  $42.9^\circ$  and  $53.1^\circ$ , corresponding to (100) and (004) plane (97). The prominent peak at  $25.7^\circ$  was assigned to the (002) plane, accommodating of an increasing in crystallinity that represent the overlapping of PANI and CNT. The XRD results in this work show consistent with the report in literature that compared the XRD pattern between PANI with PANI composited with multi-walled CNT (MWCNT). The researchers reported the relative intensity and sharpness of the peaks that was increased with an adding of MWCNT (92). All of the characterization results by IR, Raman and XRD clearly confirm that the composite of PANI and CNT powder was successfully synthesized.

Table 7 The ATR-IR peaks identification list of PANI and PANI/CNT

| Wavenumber ( $\text{cm}^{-1}$ ) |                       | Characteristic bond |
|---------------------------------|-----------------------|---------------------|
| PANI powder                     | PANI/CNT powder       |                     |
| 3450 $\text{cm}^{-1}$           | 3452 $\text{cm}^{-1}$ | N-H stretching      |
| 2925 $\text{cm}^{-1}$           | 2924 $\text{cm}^{-1}$ | C-H stretching      |
| 1598 $\text{cm}^{-1}$           | 1553 $\text{cm}^{-1}$ | C=C stretching      |
| 1465 $\text{cm}^{-1}$           | 1482 $\text{cm}^{-1}$ | C=N stretching      |
| 1295 $\text{cm}^{-1}$           | 1288 $\text{cm}^{-1}$ | C-N stretching      |
| 1115 $\text{cm}^{-1}$           | 1115 $\text{cm}^{-1}$ | C-H bending         |
| 805 $\text{cm}^{-1}$            | 806 $\text{cm}^{-1}$  | C-H bending         |

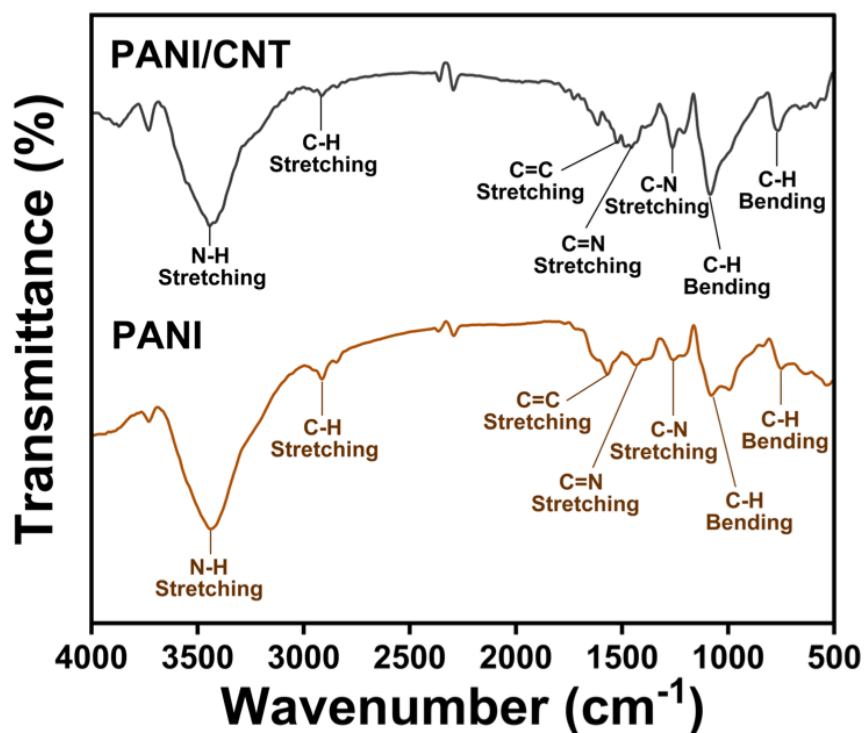


Figure 75 The ATR-IR spectra of as-prepared PANI and PANI/CNT powders

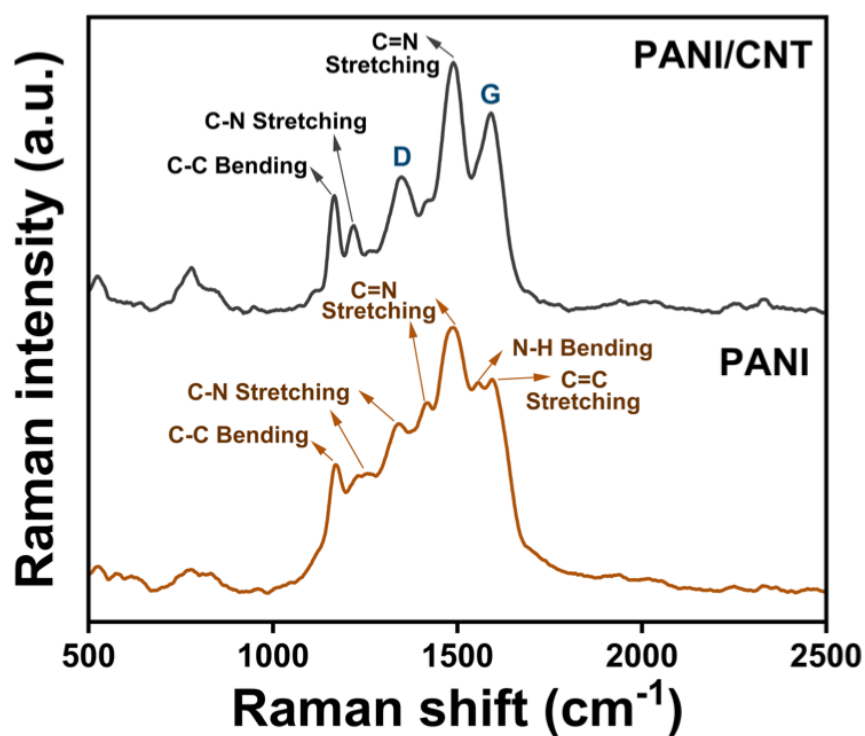


Figure 76 The Raman spectra of as-prepared PANI and PANI/CNT powders

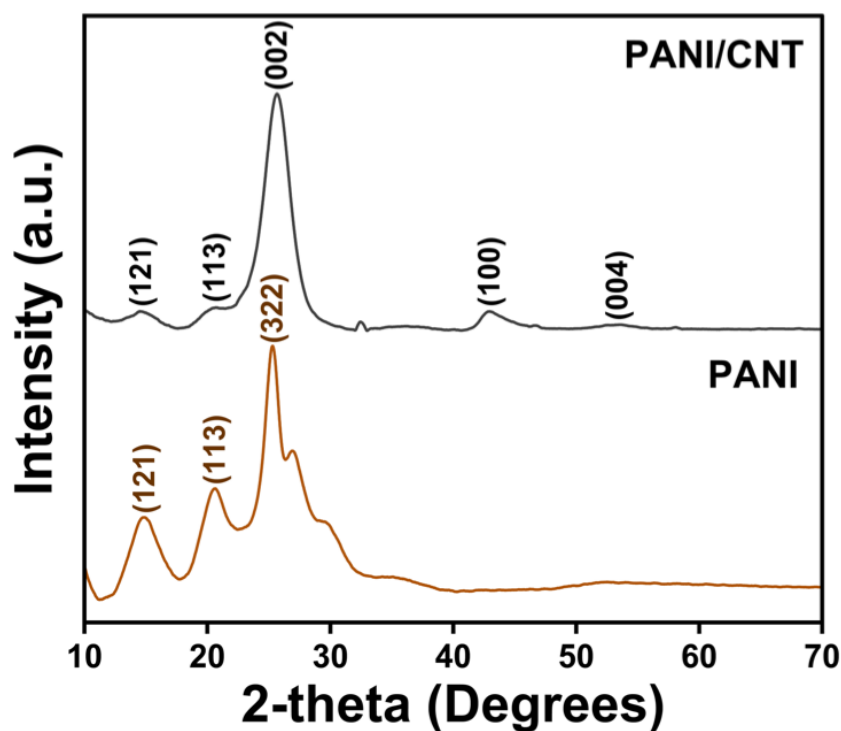


Figure 77 The XRD pattern of as-prepared PANI and PANI/CNT powders

After the study of morphology and chemical structure of PANI and PANI/CNT powder, the cellulose-based fabric/conductive polymers composites were prepared. For the PANI and PANI/CNT system, two kinds of cellulose-based fabrics consisting of Rayon and cotton fabric were selected, due to their common use and flexibility. In the next part, the physical, morphological and chemical characteristics of cellulose-based fabrics and cellulose-based fabric/PANI examined by color spectrophotometer, LOM, SEM, SR-XTM, IR, Raman and XRD techniques are reported. The scientific discussion is focused on the physical properties, surface morphology, filler particle distribution and chemical functional groups and bonding within cellulose-based fabrics compare with cellulose-based fabric/PANI by starting with Rayon following by cotton fabric systems.

#### 4.2.2 Characterization of Rayon/PANI composite fabrics

After the morphology and chemical structural of PANI powder were characterized, the Rayon fabric composite with conductive polymers of PANI powder within various conditions were prepared by ultra-sonication process. In this section, the physical and chemical characteristics of Rayon fabrics and Rayon fabric/PANI could be examined by portable color spectrophotometer, LOM, SEM, IR, Raman and XRD techniques. Therefore, the discussion will be focused on physical properties, surface morphology, composite distribution and chemical functional groups of Rayon fabrics comparison with Rayon/PANI.

##### 4.2.2.1 Morphological characterization of Rayon fabric and Rayon/PANI composite fabrics

The digital images of Rayon fabric and Rayon/PANI fabrics of all conditions are illustrated in Figure 78. Each condition shows a different dark shade with inhomogeneous color at low concentration of PANI incorporating. Higher concentration of PANI made more homogeneous color, which means that the PANI can homogeneously exist within fabric. It also shows that as the PANI content increased from 0.05 to 0.75 g, the color of the fabrics is also darker. The darkness of the fabrics was measured by portable color spectrophotometer, presenting the  $L^*$  values, as tabulated in Table 8. The  $L^*$  of pristine Rayon about 94.5 is presented meaning to the light shade of fabric. After the Rayon fabric was composited with PANI powder, the  $L^*$  of Rayon/PANI for all condition are decreased correlating with an increasing of PANI/CNT content, as can be seen in Table 8. The Rayon/PANI 0.75 g obtains the darkness color compared to other due to the largest amount of composite dark green PANI powder, corresponding to the lowest  $L^*$  in this system. Additionally, flexibility is one of the important properties for fabric materials. Figure 78b displays the digital images showing flexibility of pristine Rayon by comparing with Rayon/PANI fabrics in Figure 78c. Both of them showed the ability of folding, rolling and twisting that could be returned to the initial

state after testing. Therefore, compositing with PANI to Rayon still maintains the fabric flexibility without destroying the fabric structure.

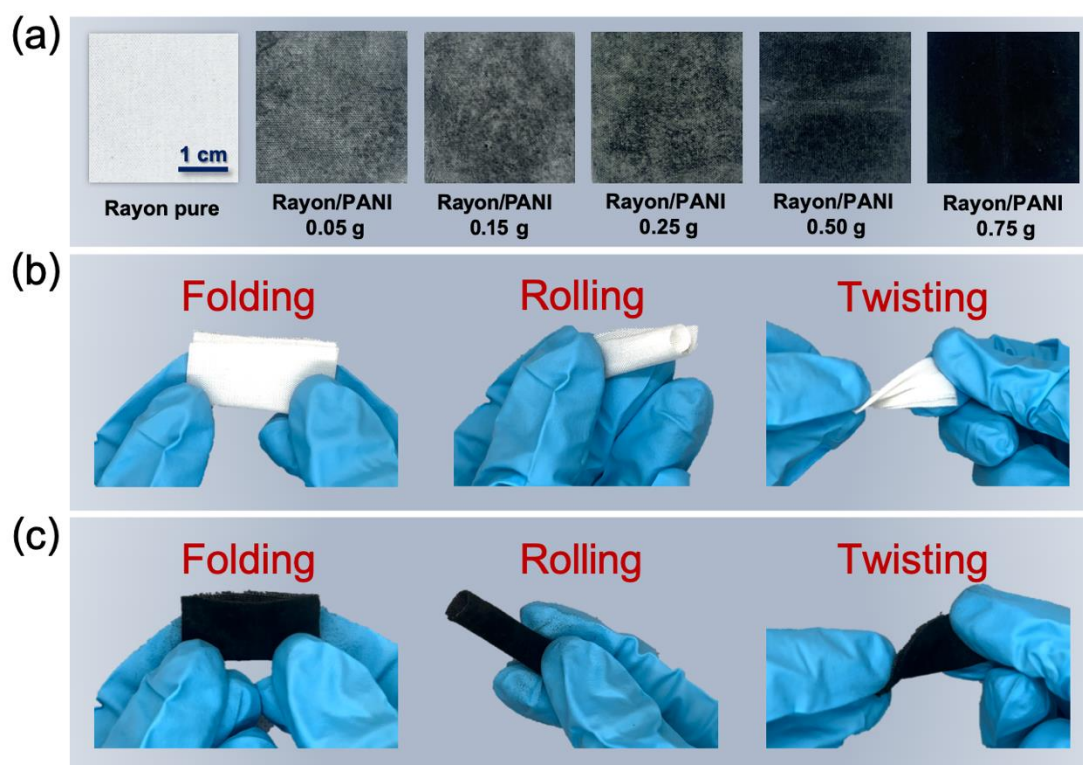


Figure 78 The digital images of (a) Rayon and Rayon/PANI in various condition (0.05, 0.15, 0.25, 0.50 and 0.75 g), and the flexibility of (b) pristine Rayon fabric and (c) Rayon/PANI composite fabric at 0.75 g of condition.

Table 8 Lightness measurement value of Rayon fabric and Rayon/PANI fabric

| Fabrics      | PANI content | D65  |
|--------------|--------------|------|
|              |              | L*   |
| Rayon fabric | 0 g          | 94.5 |
|              | 0.05 g       | 45.9 |
|              | 0.15 g       | 37.2 |
|              | 0.25 g       | 23.8 |
|              | 0.50 g       | 16.0 |
|              | 0.75 g       | 15.8 |

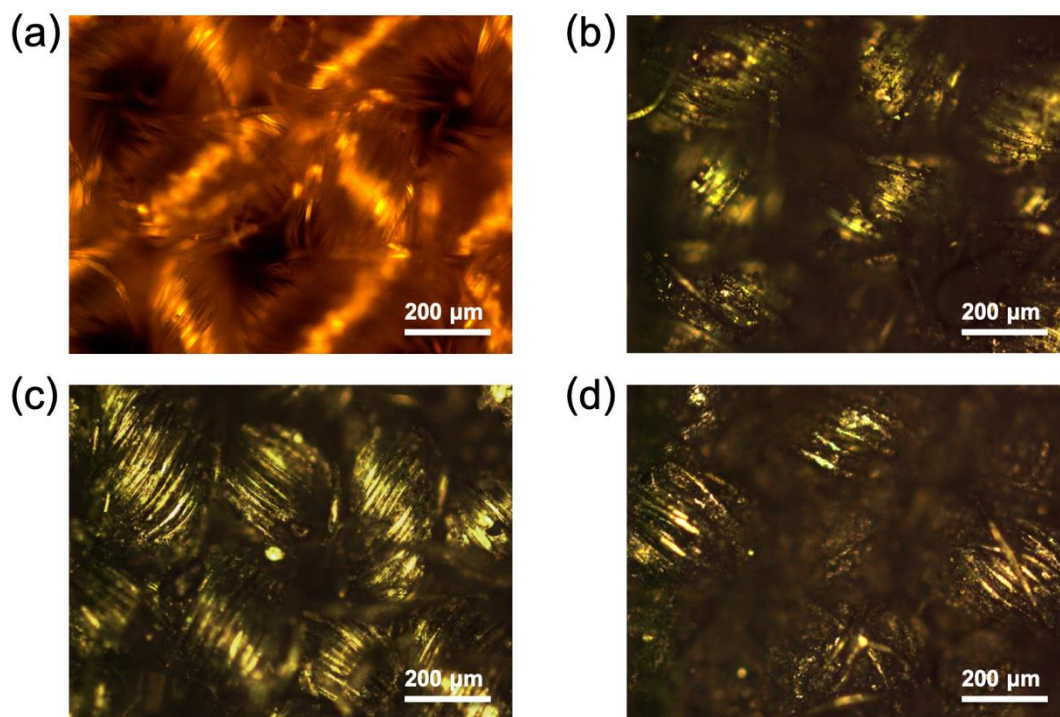


Figure 79 The light optical microscopy at 100x magnification of (a) Rayon fabric compare with Rayon/PANI (b) 0.05 g (c) 0.25 g and (d) 0.75 g.

Next, the surface morphology was observed by LOM and SEM for scientific discussion. According to Figure 79a-d, the LOM images at 100x magnification exhibit the surface morphology of Rayon and various condition of Rayon/PANI fabrics. Figure 79a presents the LOM image of Rayon fabric which shows the arrangement of Rayon fiber with orderly pattern and some porous structure. Whereas, the Rayon fabric composited PANI powder 0.05 g shows the small dark green powder dispersing over each fiber, as shown in Figure 79b. Figure 79c presents the darker color of fabric due to a larger amount of PANI at 0.25 g incorporation. The highest condition of Rayon/PANI 0.75 g demonstrates a large amount of PANI powder that can cover almost all of the fabric surface, as can be seen in Figure 79d. The LOM results can conclude that the increasing of PANI content corresponds to a larger amount of PANI powder over the surface of Rayon fabric. For more scientific information about surface morphology, the

SEM technique was used. In Figure 80a-d, the pristine Rayon fabric demonstrates the arrangement of a plenty of fibers with an average diameter of  $13.4 \pm 0.57 \mu\text{m}$ . After the Rayon was dip-coated with PANI powder in various conditions (0.05, 0.15, 0.25, 0.50, 0.75 g), over the surface of fabrics exhibit some irregular particles. As the PANI content is increased, the larger amounts of particles also increasingly appeared in relation, according to Figure 80b-d. For more details for discussion, the SEM images were conducted at higher magnification of 1000x to obtain clear picture of fiber and PANI powder incorporation. As shown in Figure 81a-d, all of the fibers show an obviously striated surface which is a surface characteristic of Rayon fiber as same as the illustration in Figure 56a. Furthermore, the micron size PANI particles are inserted between each fiber with some agglomeration at higher condition. The LOM and SEM results confirm that PANI powder is successfully dispersed over the Rayon fabric' surface.

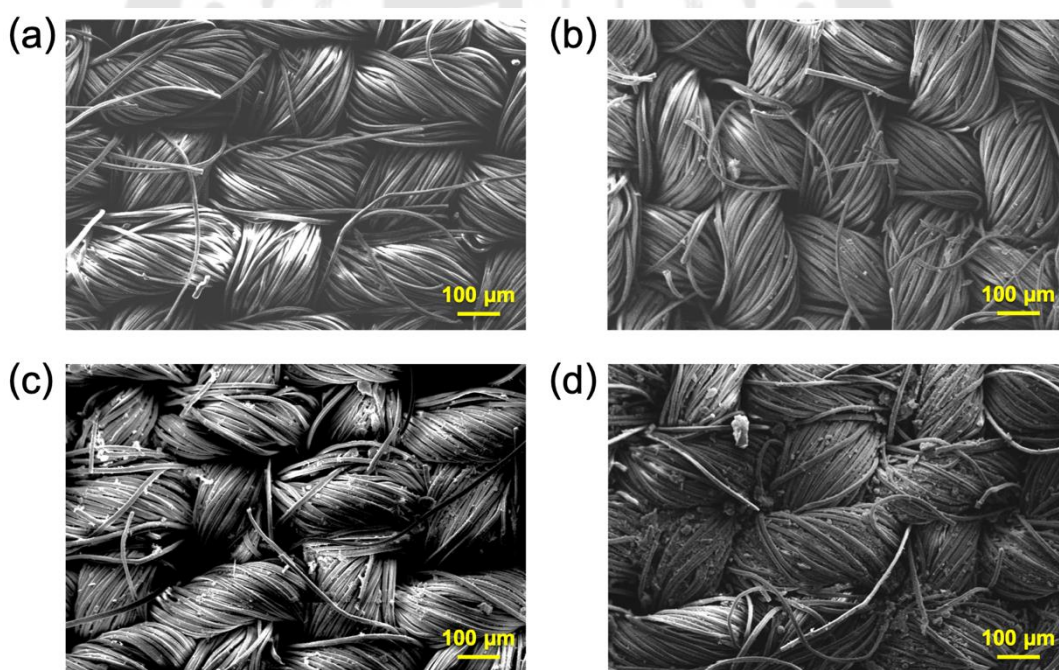


Figure 80 The SEM images of (a) Rayon fabric and Rayon/PANI (b) 0.05 g (c) 0.25 g and (d) 0.75 g at 100x magnification.

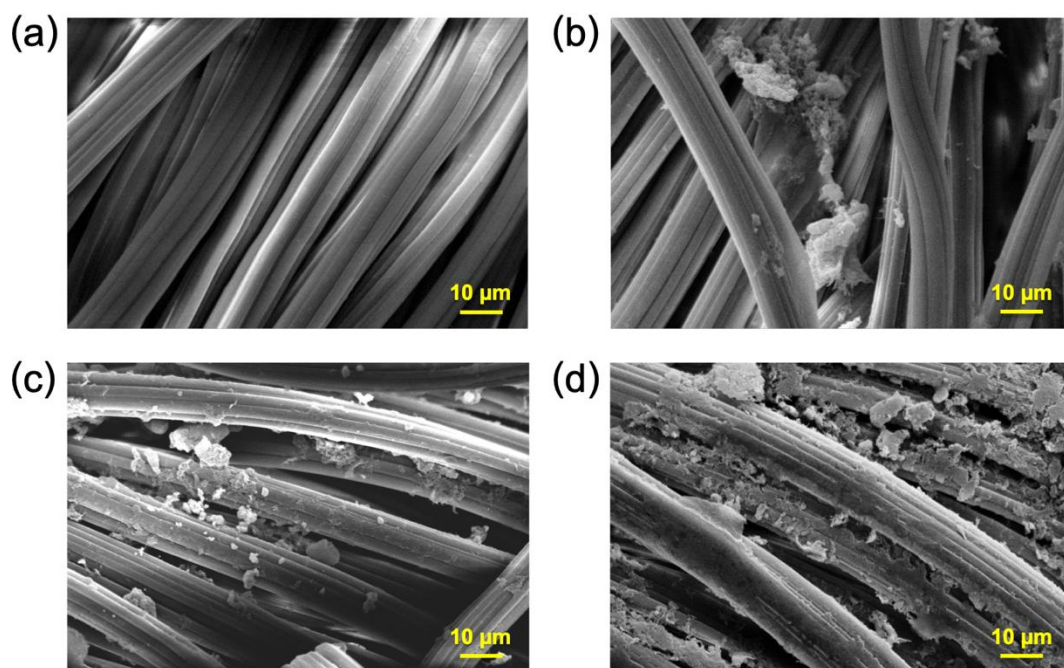


Figure 81 The SEM images of (a) Rayon fabric and Rayon/PANI (b) 0.05 g (c) 0.25 g and (d) 0.75 g at 1000x magnification.

According to LOM and SEM images of Rayon/PANI, the results presented the dispersion of PANI particles over the surface of Rayon fabric while insight the fabric structure could not see. To study the dispersibility of PANI insight the fabric structure, Synchrotron radiation X-ray tomographic microscopy (SR-XTM) technique was interesting. According to Figure 82a-c, the results exhibit a 3D visualization of Rayon composite PANI in various conditions. The structure of Rayon fabric and the distribution of PANI powder in 3D images are illustrated. The results demonstrate the dark yellow color of Rayon fabric which acts as matrix phase. The containing of the fibers in fabric structure are orderly arranged with a few of porous. Meanwhile, the filler phase of PANI powder is shown in a pink color. The 3D investigation of Rayon/PANI 0.05 g, 0.25 g and 0.75 g were compared as demonstrated in Figure 81a-c. It can be evidenced that the PANI powder not only incorporated over the fabric's surface, but also inserted deeply between each fiber and inside the Rayon structure. The larger area of PANI dispersion corresponds to an increase of PANI content. At higher content, an agglomeration

occurred illustrating the poor distribution. Thus, the SR-XTM results confirm the incorporation between Rayon fabric and PANI powders as Rayon/PANI fabric.

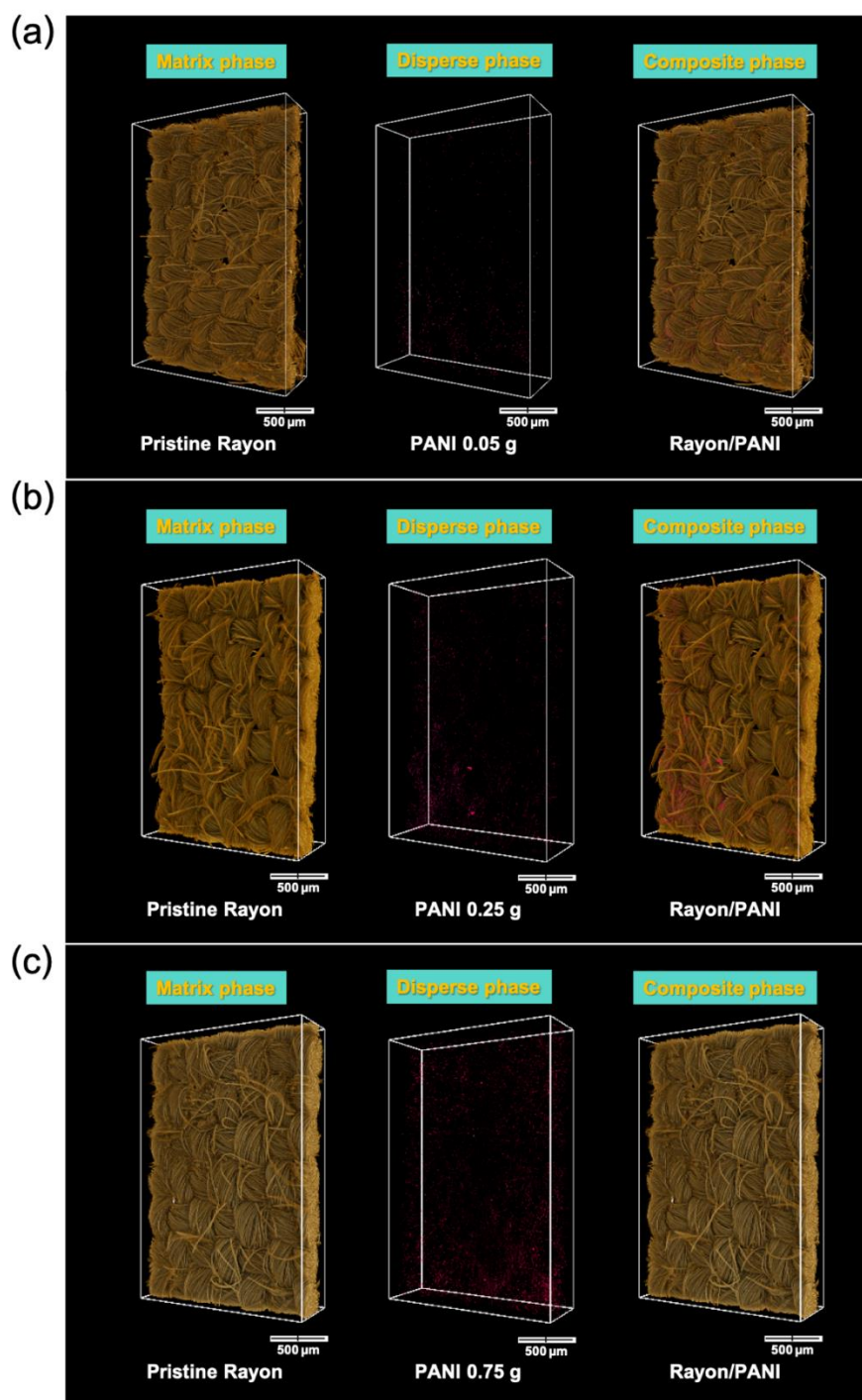


Figure 82 The 3D visualization from SR-XTM technique of Rayon/PANI at (a) 0.05 g, (b) 0.25 g and (c) 0.75 g conditions.

#### 4.2.2.2 Chemical structure characterization of Rayon fabric and Rayon/PANI composite fabrics

The chemical structural characterization is an important section to support the success of the composite fabric between Rayon and PANI powders. The chemical characterization of Rayon fabric and Rayon/PANI fabric was analyzed by ATR-IR and XRD. As shown in Figure 83, the ATR-IR spectra presented the characteristic of Rayon compared with Rayon/PANI, as identify in a range of 4000-700  $\text{cm}^{-1}$ . The stretching vibration of -OH group and C-H group was observed at 3308  $\text{cm}^{-1}$  and 2870  $\text{cm}^{-1}$ , due to the cellulose functional group of hydroxyls. The evident peaks at 1575  $\text{cm}^{-1}$  and 1299  $\text{cm}^{-1}$  of Rayon assign to O-H and  $\text{CH}_2$  group of bending vibration, corresponding to glucose unit of cellulose structure (70). Also, a strong peak at 1023  $\text{cm}^{-1}$  belongs to the C-O-C stretching. All of the peaks of Rayon fabric (Red line) indicate the characteristic of cellulose molecular structure. Meanwhile, the Rayon/PANI for various conditions shows all of vibrational peaks similar to the characteristic peaks of Rayon, the IR characteristics of PANI molecule did not appear. To confirm the composite of Rayon/PANI, XRD technique was suggested. According to Figure 84, the XRD patterns of Rayon were compared between Rayon/PANI and PANI powder. The characteristic cellulose II structure was exhibited at  $2\theta$  of  $13^\circ$  and  $20.5^\circ$ . This two peaks belong to (110) and  $(11\bar{0})$  crystal planes which corresponding to the existence of regenerated cellulose in Rayon structure (100). Also, the peaks at  $64.5^\circ$  and  $82^\circ$  are assigned to the (040) and (202) plane (101). Additionally, the XRD patterns of Rayon/PANI in all conditions are being considered. Most of the peaks of Rayon/PANI at 0.05 g condition demonstrate the Rayon characteristics. Meanwhile, the characteristic peaks of PANI are also observed within Rayon/PANI 0.25 g and 0.75 g patterns, as pointed out at  $2\theta$  of  $21.2^\circ$  and  $21^\circ$ . The prominent peaks at (113) plane corresponds to the crystalline part in the semi-crystalline PANI structure (98). Containing two diffraction patterns of cellulose and PANI in the XRD patterns can clearly confirm that the Rayon fabric composite with PANI was successfully prepared.

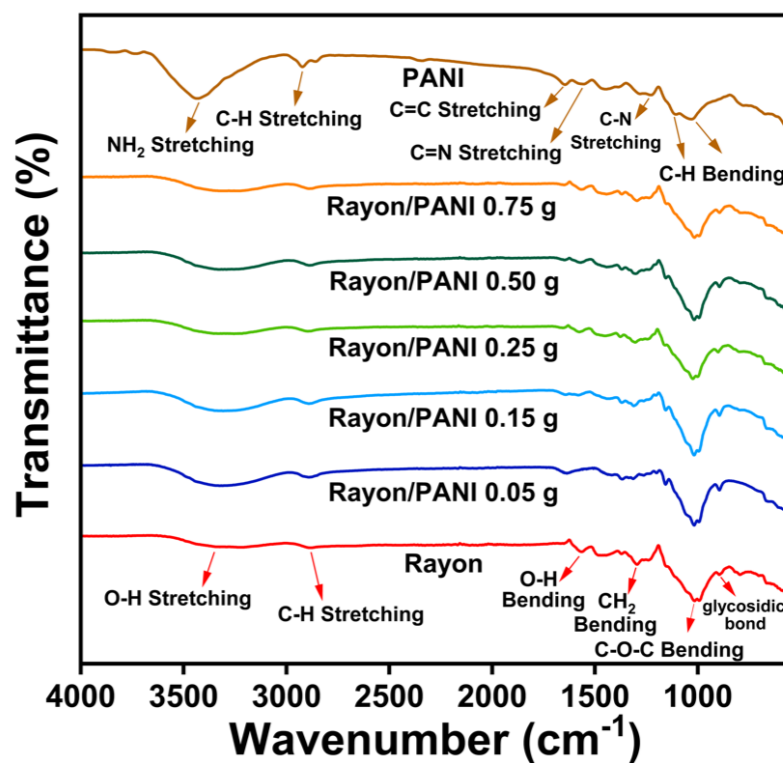


Figure 83 The ATR-IR spectra of Rayon compare with Rayon/PANI

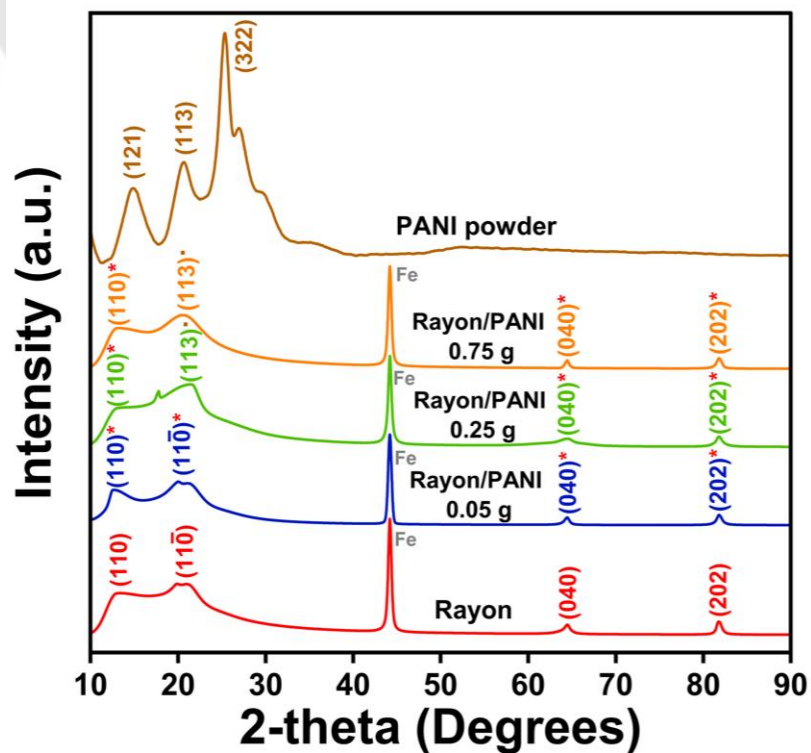


Figure 84 The XRD pattern of Rayon compare with Rayon/PANI

### 4.2.3 The electrical properties and output efficiency of Rayon fabrics and Rayon/PANI composite fabrics

#### 4.2.3.1 The electrical properties of Rayon fabrics and Rayon/PANI composite fabrics

The electrical properties consist of the impedance and electrical conductivity was analyzed in relation with frequency by using LCR meter. The results are shown in Figure 85-86. The impedance ( $Z$ ) was plotted with the relationship of the imaginary part of impedance ( $Z''$ ) and the real part of impedance ( $Z'$ ) as a function of various conditions of PANI (71). According to Figure 85, the semi-circular loops of Rayon/PANI for all conditions (0.05, 0.15, 0.25, 0.50 and 0.75 g) was plotted as same as in the work of A. Aamir et.al. (102). In each loop, the different resistivity was represented with difference in diameter. Pristine Rayon fabric (Red line) exhibits the highest resistivity with the largest loop's diameter. Meanwhile, the impedance of Rayon fabric was compared with Rayon/PANI composite fabrics. The Rayon/PANI 0.25 g (light green line) shows a nearby loop with pristine Rayon, followed by Rayon/PANI 0.15 g's loop. Conversely, the smallest in diameter's loop was given to the Rayon/PANI 0.50 g (dark green line). Whereas the semi-circular loop was expanded for more details of impedance results. It was clearly seen that the impedance values of Rayon/PANI for all conditions are slightly changed. The results reported the reducing of the loop's diameter does not depend on an increasing of PANI content. The resistivity expressed from high to low correlating to the additional amount of PANI from least to greatest. Except for the Rayon/PANI 0.25 and 0.50 g significantly show an inconstant loop, as demonstrated in Figure 86.

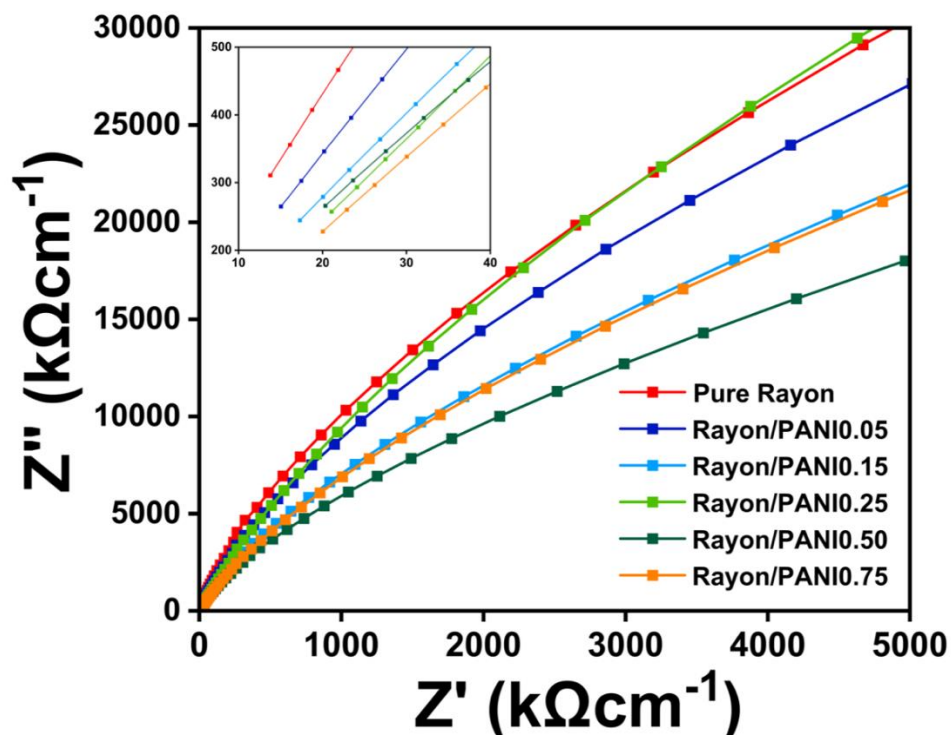


Figure 85 The impedance analysis illustrates the Nyquist plots in the function of the  $Z''$  impedance and the  $Z'$  impedance of Rayon/PANI fabric for all conditions

To confirm the trend of impedance, the electrical conductivity was analyzed along with the impedance. The electrical conductivity of Rayon/PANI fabrics are relative with a range of frequencies from 1K to 1M Hz, as shown in Figure 85. At high frequency, the conductivity of both pristine Rayon fabric and Rayon/PANI fabric for all conditions (0.05, 0.15, 0.25, 0.50 and 0.75 g) rise in the exponential trend. This result exhibits that the pristine Rayon fabric provides the lowest conductivity values of  $4 \times 10^{-6}$  S/cm, while the highest was generated by Rayon/PANI 0.75 g at  $> 5 \times 10^{-6}$  S/cm. However, the other conditions of composite fabrics not behaved to the relation of increasing content of PANI. Also, the trend of conductivity results does not correlate with the impedance trend. It can be concluded that the additional of PANI to Rayon fabrics can improve the electrical properties including the impedance and electrical conductivity, but the increasing amount of PANI in this system are inconsistent to the increased of

conductivity values. So, the study of electrical output performance is introduced for clearer reasons.

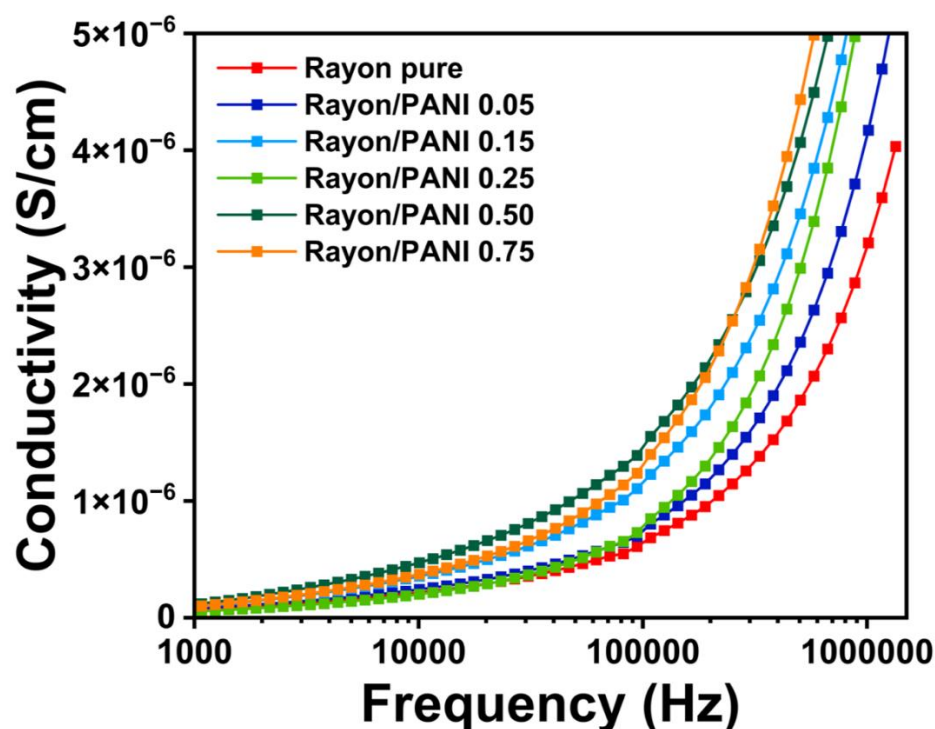


Figure 86 The electrical conductivity of Rayon/PANI for all composition (0.05, 0.15, 0.25, 0.50 and 0.75 g)

#### 4.2.3.2 The electrical working mechanism of Rayon/PANI composite fabric hybrid TENG-TEG device

The working mechanism and structural of cellulose-based fabric/PANI hybrid TENG-TEG system demonstrate as same as the Rayon/P3HT hybrid TENG-TEG system. The structure of device consists of two different tribo-materials, where tribo-positively contact layer (upper part) is fabric composite with PANI thermoelectric materials and Teflon film act as tribo-negatively contact layer. Both sides of tribo-materials attached with conductive fabric and Al tape, functioning as electrode. These two layers were placed along each other parallelly. The device was represented as Rayon/P3HT hybrid triboelectric-thermoelectric nanogenerator (Hybrid-TENG-TEG) within operation mechanism of lateral-sliding mode (LS-mode). The details of LS-mode

TENG mechanism were explained in Figure 87. In the initial state, the two tribo-materials layers are pasted in parallel direction with full of contact, generating the triboelectric charges on each material surface. The fabric/PANI produces positive charges due to the electron donating ability, while the Teflon film exhibits the electron accepting behavior, creating the negative charges. Meanwhile, the neutral without any charges transfer was demonstrated in this state owing to the creation of both charges equally. During the sliding motion was constructed, the upper layer of fabric/PANI start sliding outward until fully motion (state I-II). The unbalance of triboelectric charges of the layers occurred and induced the opposite charges to both electrodes. The top electrode of conductive fabric generates negative charges and migrates to Al tape of bottom electrode which contain positive charges. A potential difference is then created and driven the electron to export throughout the external load, producing the signal of positive current. Consequently, the motion is ongoing slide inward as shown in state III-IV with a few of the layer's surface remain connected, facilitating the continuous flow of charges. The charges from the bottom electrode move backward to the top electrode and continuously in flowing current in an opposite direction of the negative current signal (86). Resulting in an alternating current (AC) waveform caused by the repletely sliding mechanism. However, the continuous sliding motion not only generates an electrical output but also provides secondary heat energy. Heat energy is one driving source, leading to charges loss but it can be mitigated by thermoelectric effect from the composite of PANI and PANI/CNT, multiplying the triboelectric charges. So, the charges could be generated within two effects, including the triboelectric effect and the heat conduction effect. The mechanical sliding motion between fabric/PANI fabric and Teflon film layer creates the charges performed by triboelectrification. Whereas the conduction of heat energy as seen in red zone facilitated by PANI and PANI/CNT also produced an additional of the charges. Thus, both effects capability to promote an electrical output in the hybrid TENG-TEG system.

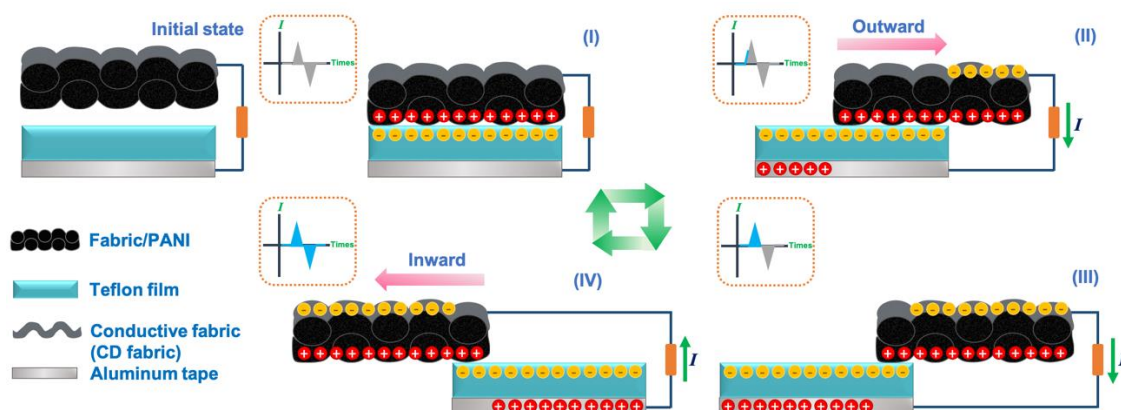


Figure 87 The working mechanism of fabric/PANI hybrid TENG-TEG within lateral sliding mode

#### 4.2.3.3 The electrical output of Rayon fabrics and Rayon/PANI composite fabric TENG-TEG devices

The electrical output including  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  of Rayon/PANI composite fabric hybrid TENG-TEG with various amounts of PANI at 0, 0.05, 0.15, 0.25, 0.50 and 0.75 g were investigated. The device was set up at room temperature within sliding mode. According to Figure 88a-b, the  $V_{OC}$  and  $I_{SC}$  demonstrate a notable increase in values when the PANI powders were composited with Rayon fabric. The  $V_{OC}$  of Rayon fabric is approximately 34.90 V and the  $I_{SC}$  is 16.0  $\mu A$ . The electrical output exhibits the rising of both  $V_{OC}$  and  $I_{SC}$  from pristine Rayon fabric to Rayon/PANI 0.25 g, reaching the best output of 45.10 V and 72.80  $\mu A$ . The results of  $V_{OC}$  and  $I_{SC}$  show 1.3 and 4.5 times higher than pristine Rayon fabric. After that, the output of  $V_{OC}$  and  $I_{SC}$  drops continuously to 36.60 V and 40.80  $\mu A$  at Rayon/P3HT 0.75 g. The results show the fluctuation of output performance where the highest output does not relate to the largest amount of PANI addition but corresponds to the suitable amount or percolation threshold in the field of composite fabrication. The percolation threshold is a critical amount of composite to matrix phase to reach an optimum electrical performance (103). After the Rayon fabric was composited with PANI, the charges carrier was generated by both triboelectrification and PANI during mechanical force applying process. The excess PANI content leads to the excess amount of charge carriers. Some charge carriers could export to external load, while the others are opposed together, leading the

charges to inappropriate to export to the external load. So, the obtained electrical output is limited. Therefore, the optimum in this Rayon/PANI system is 0.25 g of addition.

Furthermore, to support the output voltage and output current efficiency, the  $P_{max}$  of pristine Rayon fabric and Rayon/PANI was calculated as a function of varying external load resistance of  $1k\Omega$  -  $10M\Omega$ . According to Ohm's law ( $V=IR$ ), the relationship between output voltage and output current is presented in Figure 89. At higher frequencies, the voltage rises up with a drop of output current (88). The intersection points of output voltage and current represent the  $P_{max}$ , corresponding to a specific load resistance of matching external and internal load resistance. Both pristine Rayon and Rayon/P3HT 0.25 g have a specific load resistance at  $1M\Omega$ . The pristine Rayon fabric indicates  $P_{max}$  of  $114.50 \mu W$ , as depicted above in Figure 72a. The Rayon/PANI 0.25 g achieve the  $P_{max}$  of  $171.12 \mu W$  which is 1.5 times higher value than that of pristine Rayon fabric.

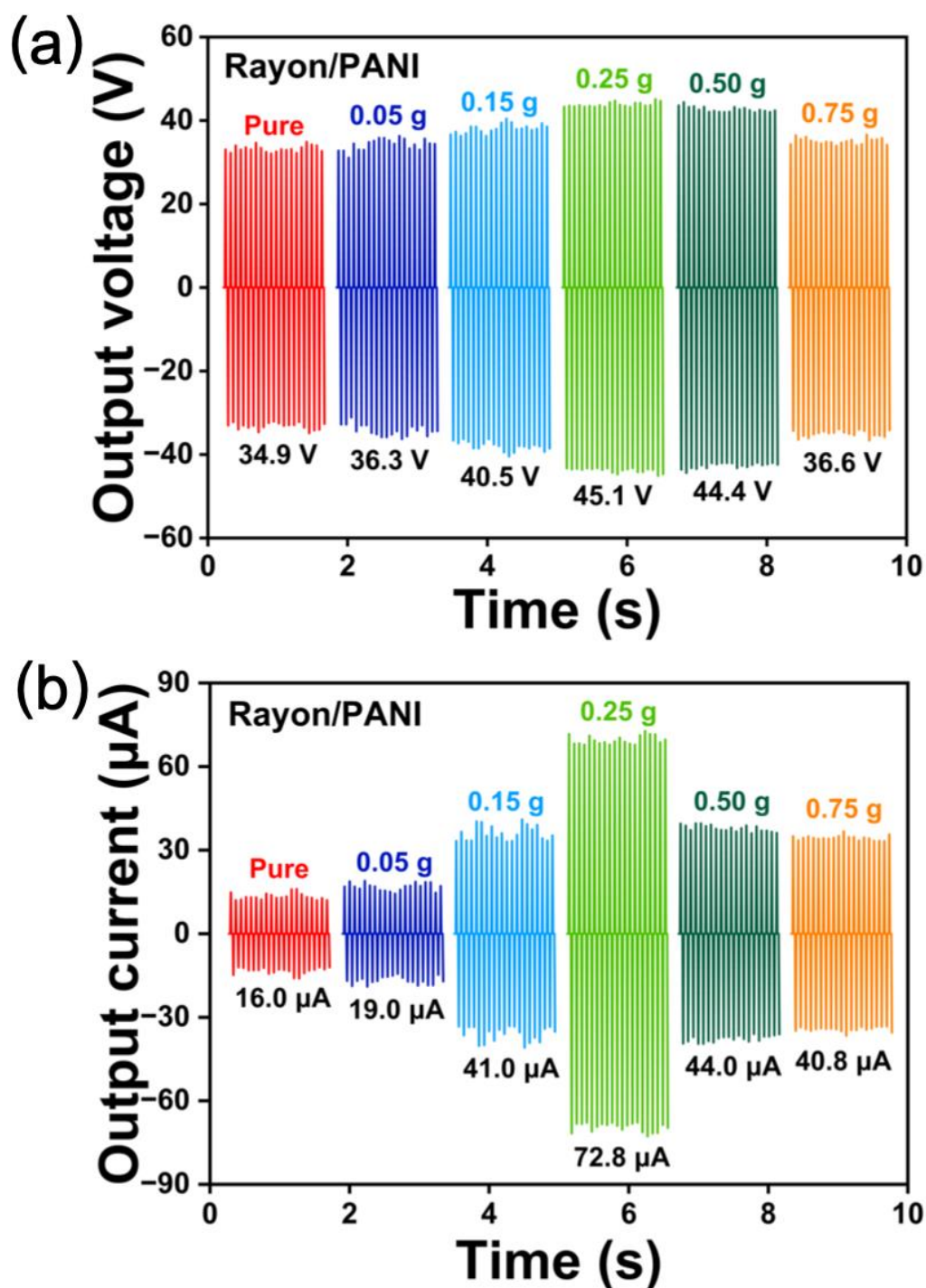


Figure 88 The electrical output performance including (a)  $V_{OC}$  and (b)  $I_{SC}$  of Rayon/PANI hybrid TENG-TEG device with varying PANI amount (0, 0.05, 0.15, 0.25, 0.50 and 0.75g)

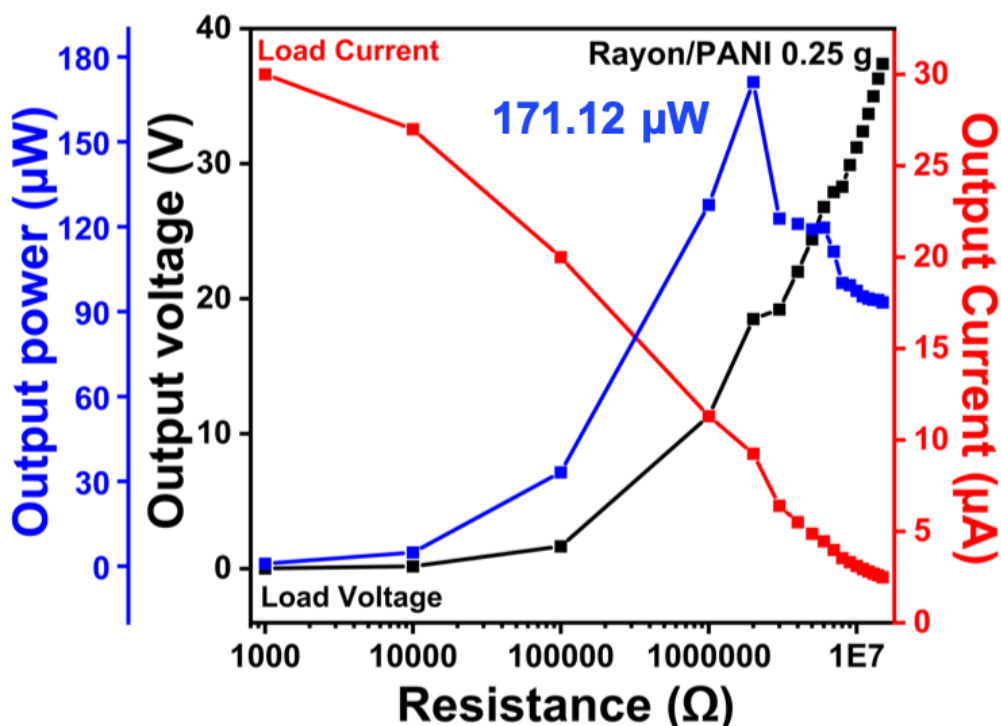


Figure 89 Maximum output power of Rayon/PANI 0.25 g under the load resistance of  $1\text{k}\Omega$  to  $10\text{M}\Omega$

To improve the electrical performance of fabric/conductive polymers, the CNT was used to composite with conductive polymers owing to their high electrical conductivity (104). So, the Rayon/PANI are expected to form three phases composite for improving the electrical output performance of hybrid TENG-TEG system. Unfortunately, the PANI/CNT show irregular dispersion on Rayon fabric. The homogeneous Rayon/PANI/CNT composite fabrics could not be prepared. Even though the additional amounts of PANI/CNT condition have been increased, the homogeneous distribution of PANI/CNT fillers is still incomplete, as depicted in Figure 90. The reason for this limitation is given to the particle's size of PANI/CNT, which is quite large, as demonstrated by SEM images in Figure 74c-d. So, the PANI/CNT particles fail to insert between the porous structure of Rayon fabric. Also, according to the smooth texture of Rayon fabric's surface, the PANI/CNT particles were unable to be completely coated. Therefore, the cotton, another type of cellulose-based fabric (105), was selected for attempting to composite with PANI and PANI/CNT to solve the problem of coating ability.

The PANI/cotton composite fabric was used to be successfully prepared by Z. Zhou and J. Sun (106), showing the opportunity to combine with CNT and provide homogeneously coating of PANI/CNT on its surface. In the next part, the results of cotton/PANI and cotton/PANI/CNT three phases' systems are illustrated and discussed.



Figure 90 The digital images of pristine Rayon fabric and Rayon/PANI/CNT in various condition (0.05, 0.15, 0.25, 0.50 and 0.75 g)

#### 4.2.4 Characterization of cotton/PANI composite fabric

As mentioned above, the two kinds of cellulose-based fabrics/PANI were studied. The cotton fabric was selected for playing with PANI and PANI/CNT compositing because of the experimental problem that happened with the Rayon systems as explained in previous section.

##### 4.2.4.1 Morphological of cotton/PANI composite fabrics

The digital images of cotton fabric and cotton/PANI fabrics are shown in Figure 91a. They demonstrate a different shade of a black color which relates to the various PANI/CNT contents. The scientific discussion of a different shade of fabric's color was presented in the  $L^*$  values. The  $L^*$  values of cotton/PANI were measured by color spectrophotometer. As listed in Table 9, the  $L^*$  of cotton fabric is 93.8 while the  $L^*$  of cotton/PANI (0.05, 0.15, 0.25, 0.50 and 0.75 g) composite fabrics is decreased with an increase of PANI content. The lowest  $L^*$  value of 15.5 was presented by cotton/PANI 0.75 g which shows the darkest of fabric compared with other conditions. It confirms that the darkness of cotton/PANI is demonstrated with an addition of PANI content. As digital images illustrated in Figure 89a, the physical color of cotton/PANI related to the  $L^*$  results. Furthermore, the pristine cotton fabric exhibits

flexibility by folding, rolling and twisting as shown in Figure 91b while after cotton fabrics is completely composite with PANI, they still reveal the flexibility and could turn to the initial shape without any structural destroying, as demonstrated in Figure 91c.

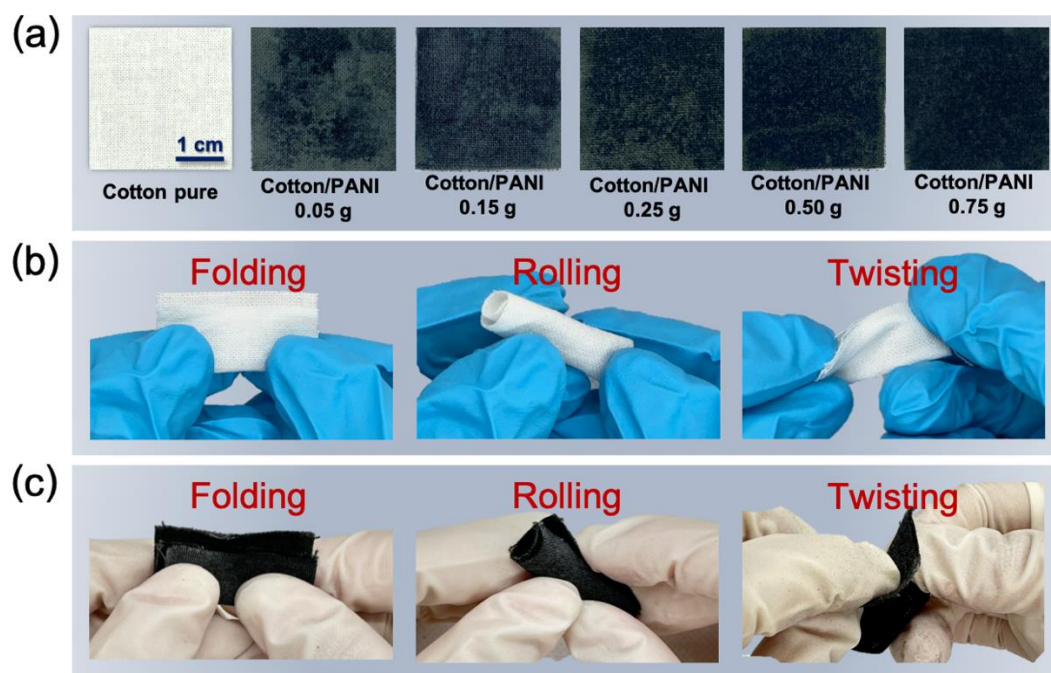


Figure 91 The digital images of (a) pristine cotton fabric and cotton/PANI in various condition (0.05, 0.15, 0.25, 0.50 and 0.75 g). The flexibility of (b) pristine cotton fabric and (c) cotton/PAN

Table 9 Lightness measurement value of cotton fabric and cotton/PANI fabric

| Fabrics       | PANI content | D65  |
|---------------|--------------|------|
|               |              | L*   |
| Cotton fabric | 0 g          | 93.8 |
|               | 0.05 g       | 21.2 |
|               | 0.15 g       | 21.0 |
|               | 0.25 g       | 20.6 |
|               | 0.50 g       | 19.3 |
|               | 0.75 g       | 15.5 |

The surface morphology of cotton fabric and cotton/PANI fabrics were examined by LOM, as shown in Figure 92. The regular arrangement of cotton fibers was illustrated in Figure 92a at 100x magnification with some of the porous structure. After the cotton fabrics were coated with PANI in various conditions, the cotton/PANI composite fabrics were demonstrated in Figure 90b-d. According to Figure 92b, the LOM image of the cotton/PANI 0.25 g shows a dispersing of PANI powder over some part of fabric's surface and between cotton fibers. Also, in Figure 92c, the cotton/PANI 0.50 g illustrates a greater amount of PANI powder that covers over the surface of cotton fabric. Moreover, the LOM images at 100x magnification of cotton/PANI 0.75 g obviously presented a greater amount of PANI powders which almost spread over the cotton fabric's surface and between the cotton fibers. Also, the PANI powder is incorporated inside the porous structure, as shown in Figure 92d. The results show that the increasing of PANI content relative to the larger amount of powder on the surface of cotton fabrics.

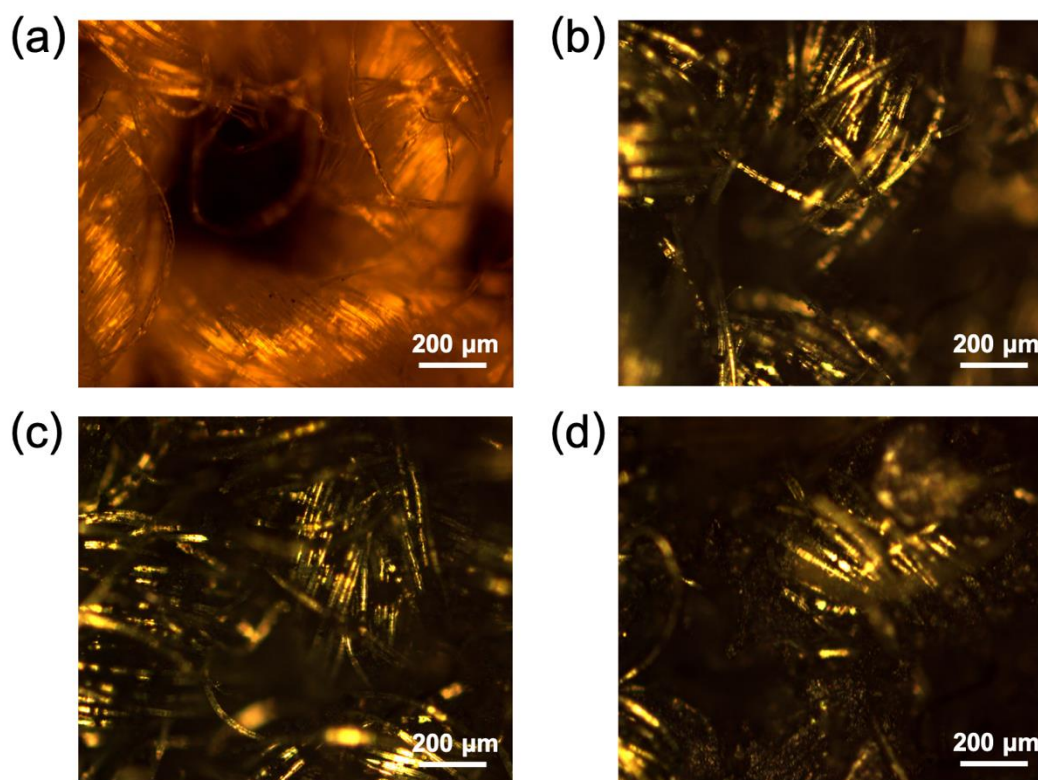


Figure 92 The light optical microscopy at 100x magnification of (a) cotton fabric compare with cotton/PANI (b) 0.05 g (c) 0.25 g and (d) 0.75 g

For more scientific discussion of surface morphology, the SEM technique was examined. According to Figure 93a, the SEM image at 2500x magnification of pristine cotton fabric was demonstrated. The SEM image shows the arrangement of cotton fibers with an average diameter size of  $10.2 \pm 0.76 \mu\text{m}$ . After the pristine cotton fabric was dip-coated with PANI powder, the surface morphology of cotton/PANI in various contents were represented in Figure 93b-d. According to Figure 93b, the PANI particle powders inserted over an arrangement of cotton fibers in cotton/PANI 0.05 g condition. A larger dispersion of PANI is related to the addition of PANI powder. As shown, the SEM images of cotton/PANI 0.25 g (Figure 93c) shows plenty of PANI particles spreading between the cotton fibers. At a higher amount of 0.75 g of PANI (Figure 93d), the PANI powders with an irregular shape are wrapped around each fiber. Moreover, it obviously shows more packing of particles with an agglomeration over the surface cotton fibers. The PANI powders are wrapped around each fiber. The SEM results can be evident that the

increasing of PANI/CNT content is relative to the larger dispersion of the PANI fillers over the cotton fiber and fabric.

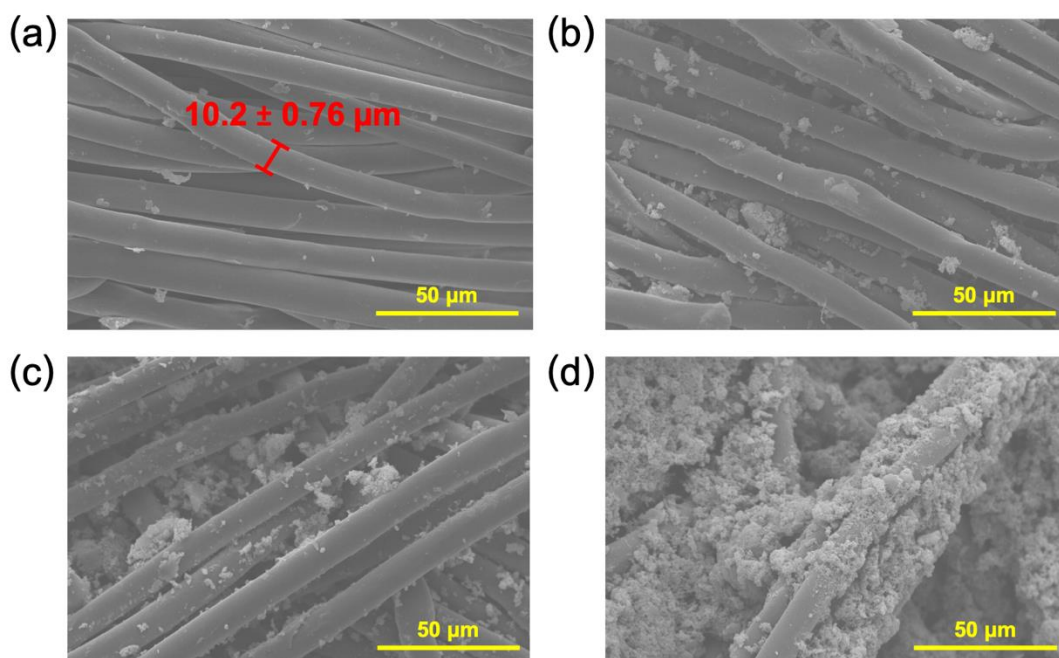


Figure 93 The SEM images of (a) cotton fabric and cotton/PANI of (b) 0.05 g (c) 0.20 g and (d) 0.75 g at 2500x magnification

#### 4.2.4.2 Chemical structure characterization of cotton/PANI composite fabrics

The chemical structure characteristic of pristine cotton and cotton-PANI fabric was examined by Raman technique in the region of 250-3500  $\text{cm}^{-1}$ . According to Figure 94, the characteristic peaks of pristine cotton shown at 633, 862 and 1298  $\text{cm}^{-1}$  are attributed to the bending and stretching vibration of C-C group, respectively. Also, the C-O-C stretching vibration corresponding to 1000 and 1096  $\text{cm}^{-1}$ . The bending vibration of C-O-H and  $\text{CH}_2$  group were observed at 1618 and 1730  $\text{cm}^{-1}$ , respectively. According to the cotton fabric after dip-coated with various condition of PANI (0.05, 0.25 and 0.75 g), could observe all characteristics of cotton and PANI. The characteristic peaks of PANI ascribe the bending vibration of N-H group at 1497  $\text{cm}^{-1}$

while the C=N stretching vibration of 1363 and 1592  $\text{cm}^{-1}$  was observed. The results show that the cotton/PANI 0.05, 0.25 and 0.75 g presented both characteristics of cotton and PANI, consisting of C-O-H,  $\text{CH}_2$  and C-C bending vibration which relate to molecular structure of cotton. Meanwhile, the N-H group of bending vibrational was also found in cotton/PANI which symbolized the P3HT characteristic. Thus, in addition to morphology characteristics, all of the spectra by Raman technique are another way to confirm the successful preparation of cotton fabric composite with PANI powder.

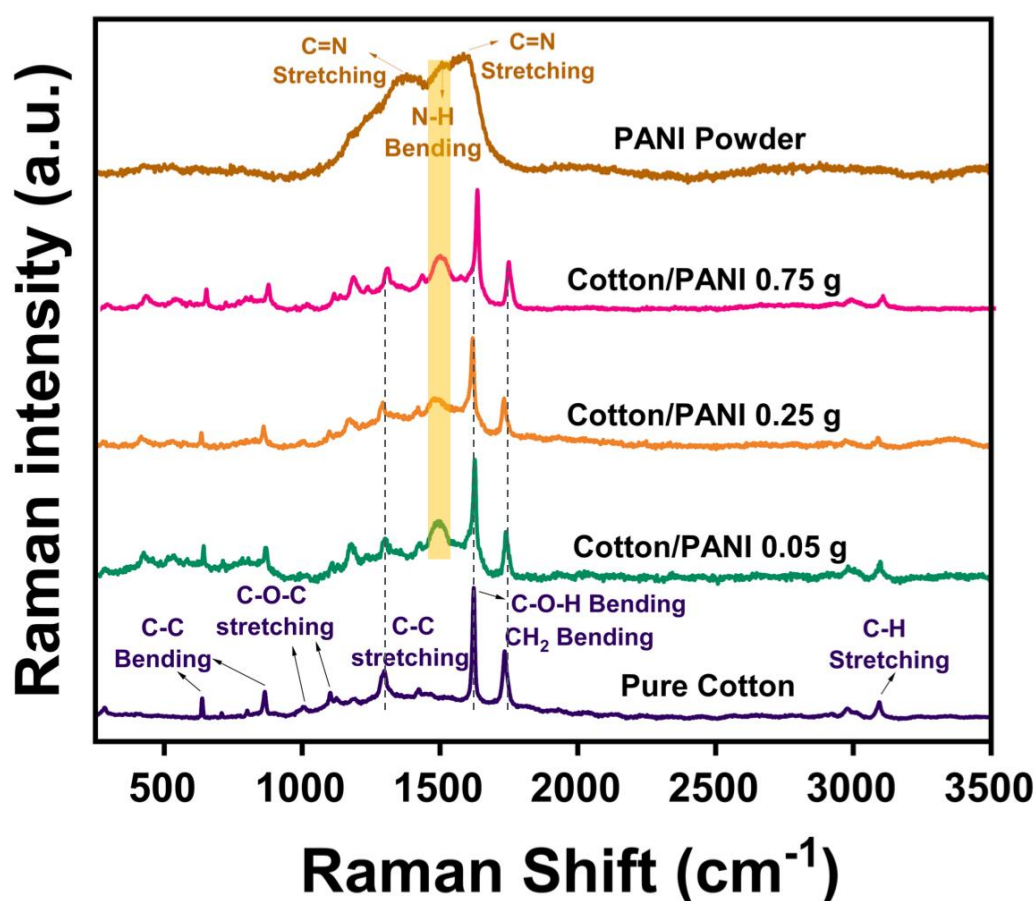


Figure 94 The Raman spectra of cotton compare with cotton/PANI

#### 4.2.5 The electrical properties and output efficiency of cotton fabrics and cotton/PANI composite fabrics

##### 4.2.5.1 The electrical properties of cotton fabrics and cotton/PANI composite fabrics

The electrical properties of the impedance and electrical conductivity were analyzed in relation to frequency by using LCR meter. As shown in Figure 95, the impedance ( $Z$ ) was plotted with the relationship of the imaginary part of impedance ( $Z''$ ) and the real part of impedance ( $Z'$ ) as a function of various conditions of PANI (71). The results reported in the form of the semi-circular loops of cotton/PANI for all conditions (0.05, 0.15, 0.25, 0.50 and 0.75 g). In each loop, the different resistivity was represented with difference in diameter. Firstly, the pristine cotton fabric (purple line) exhibits the highest resistivity with the largest loop's diameter. Also, the cotton/PANI 0.05 g shows a nearby loop of pristine cotton. Meanwhile, adding a larger amount of PANI content to the cotton fabric presented a decrease in diameter's loop. Conversely, the smallest in diameter's loop was given to the Rayon/PANI 0.75 g (pink line). The results show that the reducing of the loop's diameter depends on an increasing of PANI content. So, the Rayon/PANI 0.75 g reaches the lowest resistivity while pristine cotton reveals the highest resistivity value in this system.

The impedance could confirm the trend along with the electrical conductivity. According to Figure 96, the electrical conductivity of pristine cotton compares with cotton/PANI composite fabrics. The conductivity of cotton/PANI fabrics are relative with a range of frequencies from 1K to 1M Hz. At 1M Hz frequency, the conductivity of both pristine cotton fabric and cotton/PANI fabric rises exponential trend. The lowest conductivity of  $4.3 \times 10^{-7}$  S/cm was given by pristine cotton, while the highest was generated by cotton/PANI 0.75 g at  $2.8 \times 10^{-5}$  S/cm. All of conductivity results show the behaved exponential graph with relation to an increase of PANI contents. Moreover, the electrical conductivity results show the same tendency as with impedance results. Importantly, it can be concluded that the addition of PANI to cotton fabrics can improve the electrical properties including the impedance and electrical conductivity. So, the

study of electrical output performance is introduced to support the impedance and conductivity results.

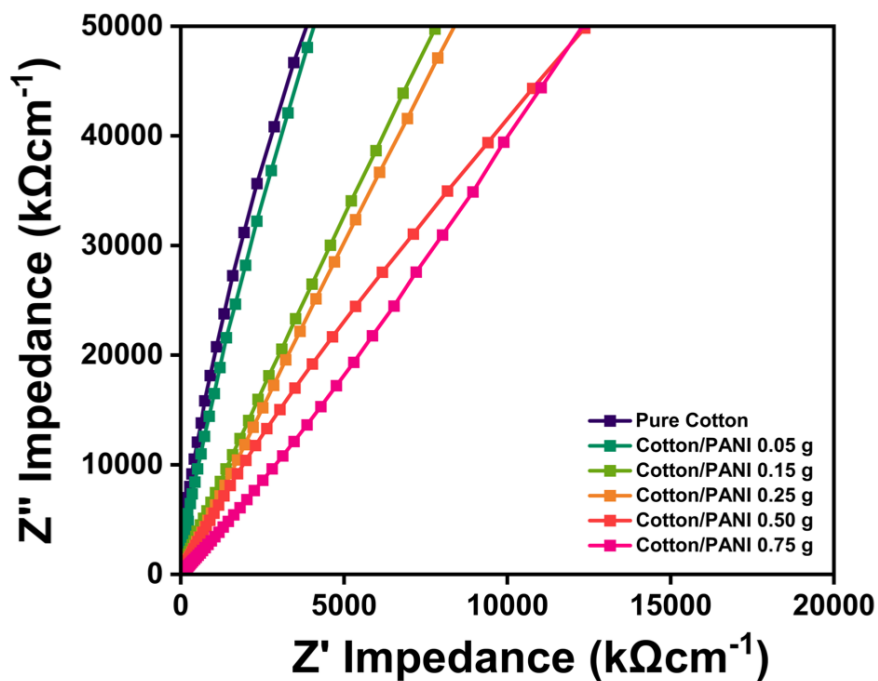


Figure 95 The impedance analysis illustrates the Nyquist plots in the function of the Z'' impedance and the Z' impedance of cotton/PANI fabric for all conditions

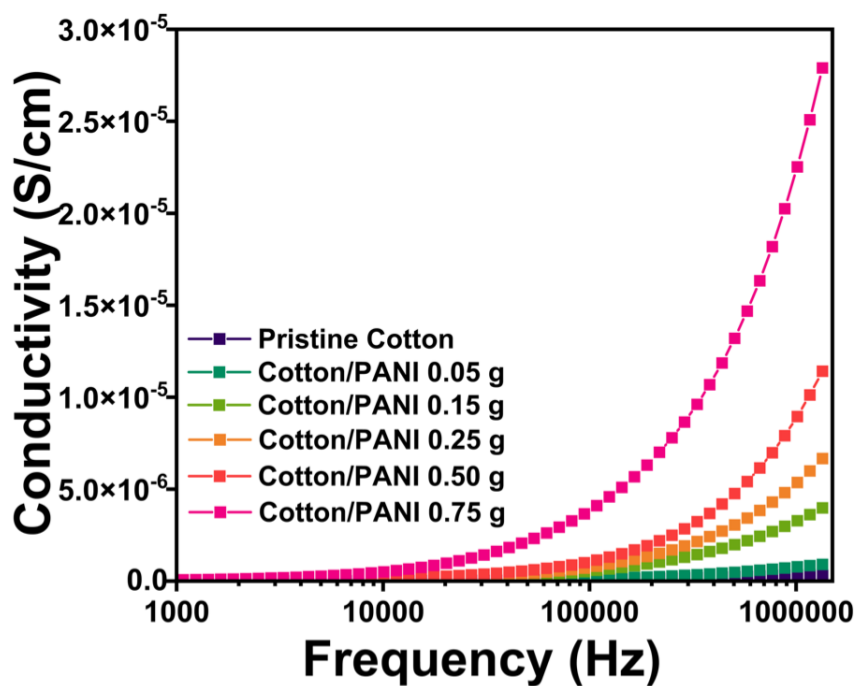


Figure 96 The electrical conductivity of cotton/PANI for all composition (0.05, 0.15, 0.25, 0.50 and 0.75 g)

#### 4.2.5.2 The working mechanism of cotton/PANI composite fabric hybrid TENG-TEG devices

The working mechanism and structural of cotton/PANI hybrid TENG-TEG system demonstrate as same as the Rayon/PANI hybrid TENG-TEG system. The structure of device consists of cotton/PANI composite fabric as tribo-positively contact layer (upper part) and Teflon film act as tribo-negatively contact layer. Both sides of tribo-materials attached with conductive fabric and Al tape, functioning as electrode. These two layers were placed along each other parallelly. The device was represented as Hybrid-TENG-TEG within LS-mode as operation mechanism. The details of LS-mode TENG mechanism were explained similarly in 4.2.3.2 section and in Figure 87. In the initial state, the two tribo-materials layers are pasted in parallel direction with full of contact, generating the triboelectric charges on each material surface. The cotton/PANI produces positive charges due to the electron donating ability, while the Teflon film exhibits the electron accepting behavior, creating the negative charges. In this state the charges are not transferred owing to the creation of both charges equally. During the sliding motion was constructed, the upper layer of fabric/PANI start sliding outward until fully motion (state I-II). The unbalance of triboelectric charges of the layers occurred and induced the opposite charges to both electrodes. A potential difference is then created and driven the electron to export throughout the external load, producing the signal of positive current. Consequently, the motion is ongoing slide inward as shown in state III-IV with a few of the layer's surface remain connected, facilitating the continuous flow of charges and current in an opposite direction of the negative current signal (86). Resulting in an alternating current (AC) waveform caused by the repletely sliding mechanism. However, the continuous sliding motion not only generates an electrical output but also provides secondary heat energy. Heat energy is one driving source, leading to charges loss but it can be mitigated by thermoelectric effect from the composite of PANI incorporating the triboelectric charges. So, the charges could be generated within two effects, including the triboelectric effect and the heat conduction effect. Thus, both effects capability to promote an electrical output in the hybrid TENG-TEG system.

#### 4.2.5.3 The electrical output performance of cotton fabrics and cotton/PANI composite fabric TENG-TEG devices

The electrical output of hybrid TENG-TEG pristine cotton and cotton/PANI fabric as a function of times with varying of PANI/CNT content (0.05, 0.15, 0.25, 0.50 and 0.75g), was compared. The electrical results of  $V_{OC}$  and  $I_{SC}$  were investigated at room temperature, according to Figure 97a-b. Pristine cotton generates the  $V_{OC}$  of 11.18 V which is the lowest value. The cotton/PANI increased from 11.18 V to 30.58 V that was given by cotton/PANI 0.05 g. Meanwhile, the cotton/PANI 0.15 g provides the highest value of  $V_{OC}$  about 34.0 V. After cotton fabric composite with higher condition of PANI powder, the  $V_{OC}$  are decreased in order. The  $V_{OC}$  of cotton/PANI at 0.25, 0.50 and 0.75 g reveal about 28.40 V, 25.77 V and 23.06 V, respectively. The  $I_{SC}$  shows the same trend as the  $V_{OC}$ , the values increase and decrease in a similar direction, as shown in Figure 97b. The  $I_{SC}$  of pristine cotton also reveal the lowest value of 38.0  $\mu$ A. Whereas the cotton with varying PANI content of 0.15 g achieved at 47.0  $\mu$ A which is the optimum values compare with other. The highest  $V_{OC}$  and  $I_{SC}$  values given to the cotton/PANI with 0.15 g which is three times larger than pristine cotton. Furthermore, to supplement the generating of the output performances, the  $P_{max}$  of pristine cotton and cotton/PANI was compared. The  $P_{max}$  was measured under the external load resistance of 1k $\Omega$  - 10M $\Omega$ . Based on Ohm's law:  $V=IR$ , while the rising of output voltage occurred with the increasing of external load resistance, the output current dropped (87). The  $P_{max}$  of pristine cotton fabric is exhibited approximately ~49.6  $\mu$ W at the external load resistance of 1M $\Omega$ . The results can be seen in Figure 98a. Whereas in Figure 98b, the cotton/PANI 0.15 g generated the  $P_{max}$  of 510.7  $\mu$ W. It demonstrates that the  $P_{max}$  of cotton/PANI obtained a higher value than that of pristine cotton by 10 times, due to composite of PANI.

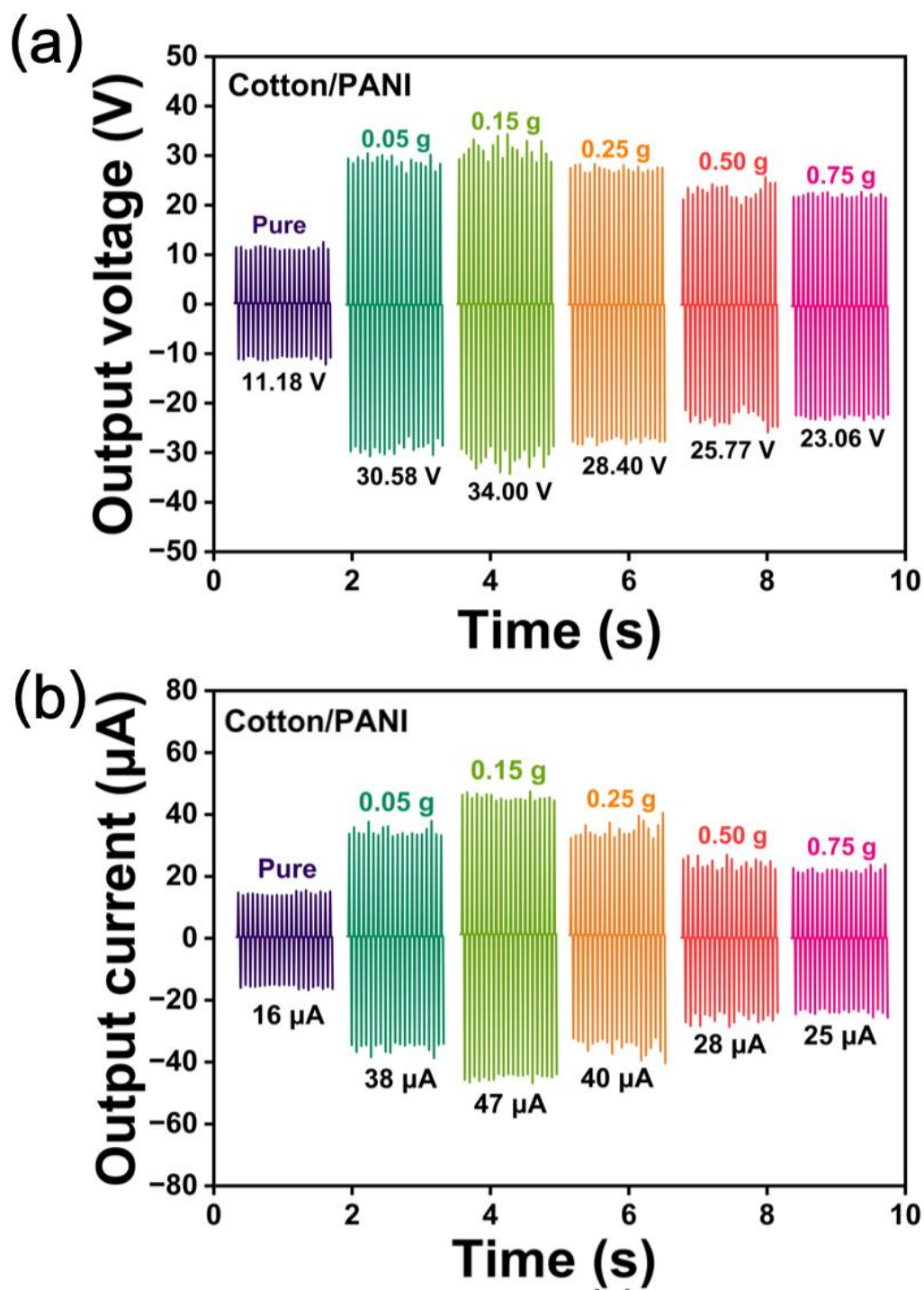


Figure 97 The electrical output performance including (a)  $V_{OC}$  and (b)  $I_{SC}$  of cotton/PANI hybrid TENG-TEG device with varying PANI amount (0, 0.05, 0.15, 0.25, 0.50 and 0.75g)

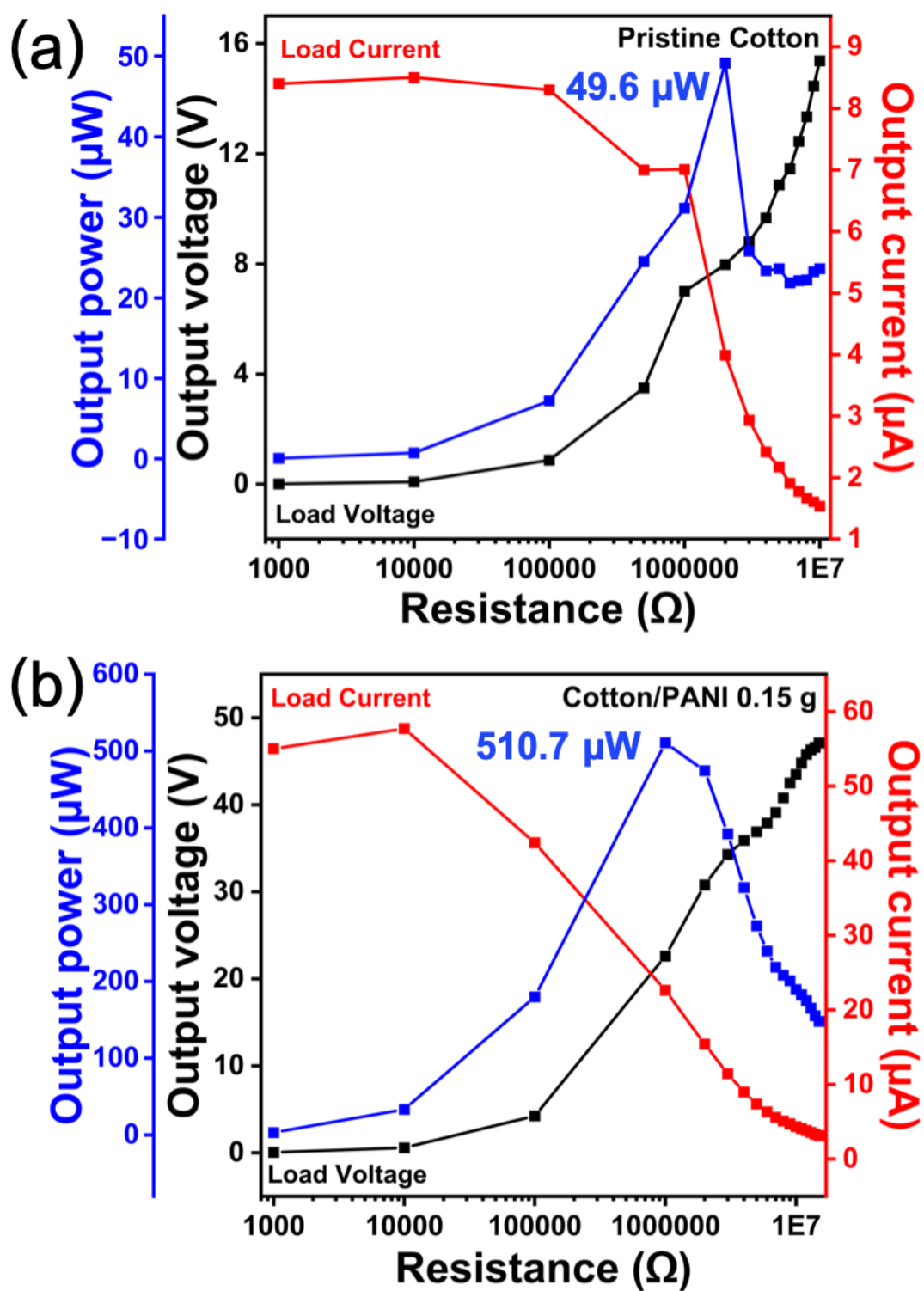


Figure 98 Maximum output power of (a) pristine cotton and (b) cotton/PANI 0.15 g under the resistance of  $1k\Omega$  -  $10M\Omega$

The results of electrical output characteristics indicated that the incorporation of mechanical energy can be an effective heat source to improve electrical output signal of Rayon/PANI and cotton/PANI hybrid TENG-TEG device. It can also be understood that besides the factor of increase in temperature, appropriate amounts of PANI are also another key factor to create suitable concentration of charge carriers. Inappropriate PANI content leads to the decreasing of output efficiency because of too much charge carriers cannot go to the external load at the same period. A reason for this effect is when the charges were excess generated, each charge will have a chance to oppose together and not export to the external load. So, the output efficiency is probably limited. The way to develop its efficiency is still open. One of them is compositing PANI conductive polymer with high electrical conductivity material, such as CNT. In addition, Rayon/PANI system demonstrate the fluctuation results between electrical properties and electrical output. The reason for these results is given to the coating ability and dispersibility of PANI particle over the Rayon fabric surface that the PANI are irregularly dispersed. The cotton, another type of cellulose-based fabric, was selected for attempting to composite with PANI/CNT as another hybrid TENG-TEG system to solve the problem of coating ability. So, the cotton-PANI/CNT are selected as another studied system for comparison.

#### 4.2.7 Characterization of cotton/PANI/CNT composite fabrics

The cotton fabric composite with conductive polymers of PANI/CNT powder within various conditions was prepared by ultra-sonication process. In this section, the physical and morphology of cotton fabrics and cotton/PANI/CNT could be examined by portable color spectrophotometer, LOM, SEM and SR-XTM. Therefore, the discussion will also be focused on chemical functional groups of cotton fabrics comparison with cotton/PANI/CNT by Raman technique.

#### 4.2.7.1 Morphological of cotton/PANI/CNT composite fabrics

According to Figure 99a, the digital images of cotton fabric and cotton-PANI/CNT fabrics are shown. The digital images demonstrate a different shade of a black color which relates to the different number of PANI/CNT contents. The  $L^*$  values of cotton/PANI/CNT by color spectrophotometer was also measured. As listed in Table 10, the  $L^*$  of cotton fabric is 93.8 while the  $L^*$  of cotton/PANI/CNT (0.05, 0.25, 0.5, 0.75, 1.00 and 1.50 g) fabrics decreased with an increase of PANI/CNT content. The cotton-PANI/CNT 1.5 g shows the lowest  $L^*$  value of 6.6 which presents the darkest of fabric compared with other conditions. It confirms that the cotton/PANI/CNT demonstrates the darkness with an addition of PANI/CNT content. The  $L^*$  results of composite fabrics correspond to the physical color of composite fabrics in digital images of Figure 98a. Additionally, the pristine cotton fabric exhibits flexibility by folding, rolling and twisting without any structural destroying as shown in Figure 99b. After the cotton fabric is completely dip-coated with PANI/CNT, they still reveal the flexibility and capability to turn to the initial shape, as demonstrated in Figure 99c.

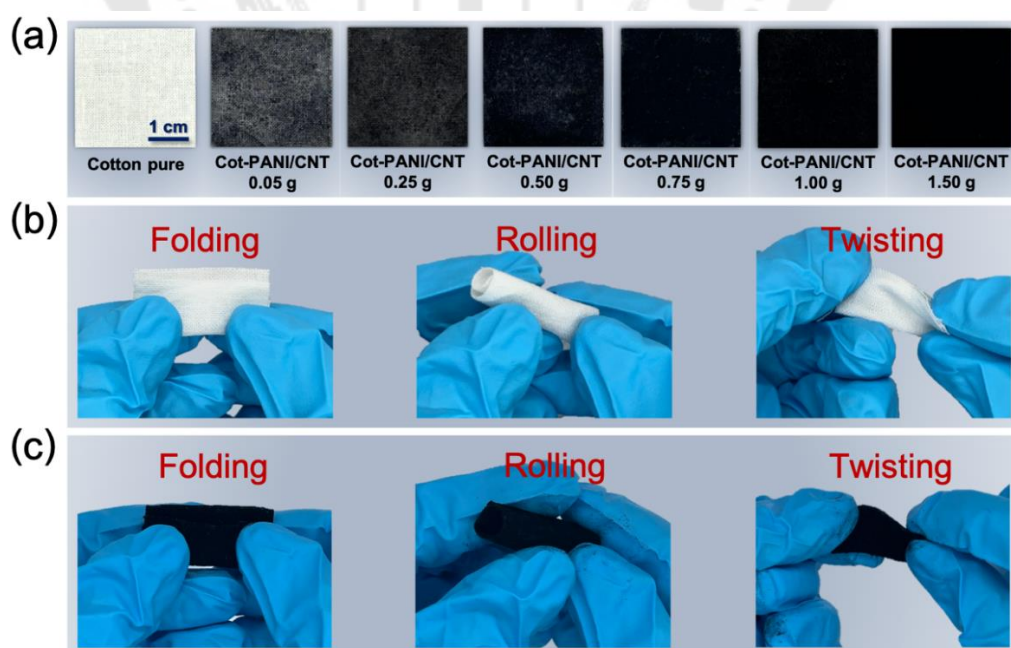


Figure 99 The digital images of (a) pristine cotton fabric and cotton/PANI/CNT in various condition (0.05, 0.25, 0.50, 0.75, 1.00 and 1.50 g). The flexibility of (b) pristine cotton fabric and (c) cotton/PANI/CNT

Table 10 Lightness measurement value of cotton fabric and cotton/PANI fabric

| Fabrics       | PANI/CNT content | D65  |
|---------------|------------------|------|
|               |                  | L *  |
| Cotton fabric | 0 g              | 93.8 |
|               | 0.05 g           | 31.3 |
|               | 0.25 g           | 12.9 |
|               | 0.50 g           | 8.5  |
|               | 0.75 g           | 8.1  |
|               | 1.00 g           | 7.7  |
|               | 1.50 g           | 6.6  |

The surface morphology of cotton fabric and cotton/PANI/CNT fabrics were examined by LOM, as shown in Figure 99. As shown in Figure 100a, the cotton fabric illustrates the cotton fibers which have regularly arranged with some of the porous structure. The cotton fabrics were coated with PANI/CNT in various conditions. According to Figure 100b, the LOM image at 100x magnification of the cotton/PANI/CNT 0.25 g shows a spreading of PANI/CNT powder on some part of fabric's surface and inside the porous structure. Also, in Figure 100c, the cotton/PANI/CNT 0.50 g illustrates more amount of PANI/CNT powder that covers over the surface of cotton fabric with some fibers have appeared. In addition, the LOM images of cotton/PANI/CNT 1.00 g obviously presented that the PANI/CNT powders are almost spread over the cotton fabric's surface including over the cotton fibers and also inside the porous structure, as shown in Figure 100d. The results show that the increasing of PANI/CNT content is relative to the larger amount of powder on the surface of cotton fabrics.

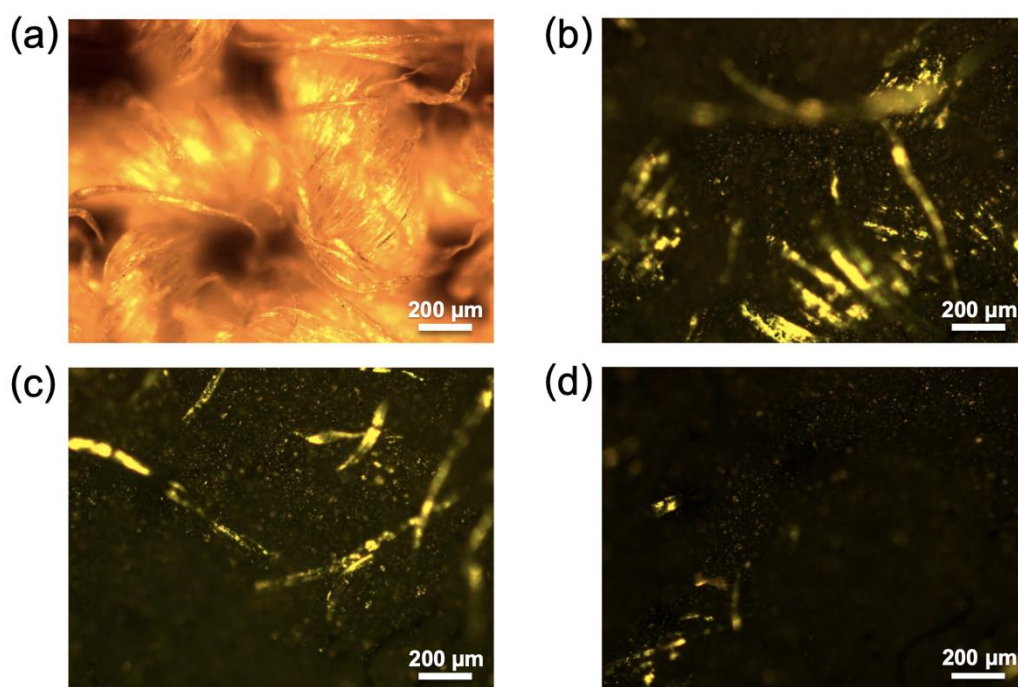


Figure 100 The light optical microscopy at 100x magnification of (a) cotton fabric compare with cotton/PANI/CNT (b) 0.25 g (c) 0.50 g and (d) 1.00 g.

For more scientific explanation of surface morphology, the SEM technique was examined. According to Figure 101a, the SEM image at 100x magnification of pristine cotton fabric was exhibited. The image shows the arrangement of cotton fibers with some of porous occurred. After the pristine cotton fabric was composited with PANI/CNT, the surface morphology of cotton/PANI/CNT in different content of PANI/CNT (Figure 101b-d) represents the existing of PANI/CNT particle powders dispersed over the cotton fibers. A larger dispersion of PANI/CNT is related to the addition of PANI/CNT powder. As can see, the SEM images cotton-PANI/CNT 0.25 g (Figure 101b) shows plenty of small PANI/CNT particles spreading over the fabric's surface. At higher conditions of 0.50 g (Figure 101c) and 1.00 g (Figure 101d) of PANI/CNT, more packing of particles over the surface and porous of fabric appeared. In addition, the SEM images were zoomed in at 500x magnification to see more details of morphology, as shown in Figure 102a-d. The pristine cotton fibers demonstrate an average diameter size of  $12.65 \pm 3.62 \mu\text{m}$ , according to Figure 102a. The comparison of the cotton/PANI/CNT between

0.25, 0.50, and 1.00 g obviously shows an increasing amount of PANI/CNT powder with an increase of the composite content. The cotton/PANI/CNT fabrics contain an agglomeration of spherical PANI/CNT particles over the surface of cotton fiber as can be seen in Figure 101b-d. According to Figure 102b, the PANI/CNT particles of 0.25 g content are inserted between an arrangement of fibers. At 0.50 g of PANI/CNT, a spreading of PANI/CNT particles are presented in larger amount (Figure 102c). Finally, at 1.00 g condition (Figure 102d), the SEM image shows the PANI/CNT particles covering all over the cotton's fibers with board size distribution. The SEM results can be evident that the increasing of PANI/CNT content is relative to the larger dispersion of the PANI/CNT fillers over the cotton fabric.

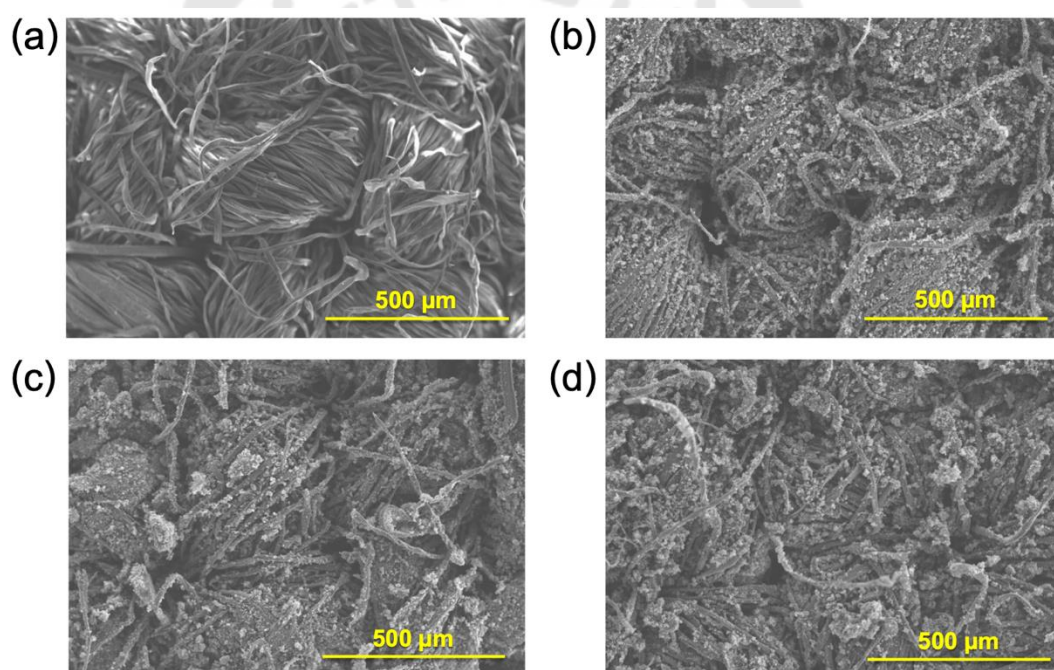


Figure 101 The SEM images of (a) cotton fabric and cotton/PANI/CNT of (b) 0.25 g (c) 0.50 g and (d) 1.00 g at 100x magnification.

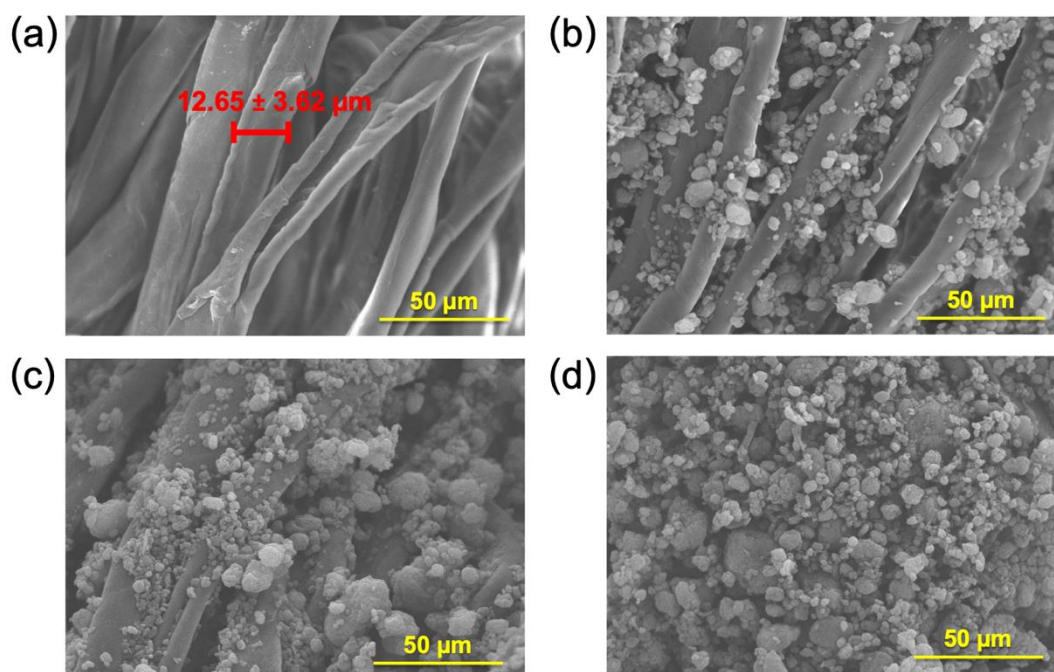


Figure 102 The SEM images of (a) cotton fabric and cotton/PANI/CNT of (b) 0.25 g (c) 0.50 g and (d) 1.00 g at 500x magnification.

In addition, the EDS analysis was investigated to analyze the elements of the PANI/CNT. The results of pristine cotton fabric and cotton/PANI/CNT 1.50 g are illustrated in Figure 103a-b, respectively. In Figure 103a, the EDS results report that element of C (Red) and element of O (Green) in weight ratio can be found, according to the containing of cellulose functional group of pristine cotton. The OH-group in chemical structure of cotton relating to the 41.13 wt% of O element while the C element display about 58.87 wt%. In Figure 103b, the composite between cotton fabric and PANI/CNT reveals an increasing amount of C atom at 87.74 wt%, which is 1.5 times higher than that of pristine cotton. The reason for larger C atom caused by the additional of the PANI and CNT disperse phases, due to the PANI and CNT are mainly composed of C atoms. So, it can conclude that the cotton fabric could dip-coated by PANI/CNT powder.

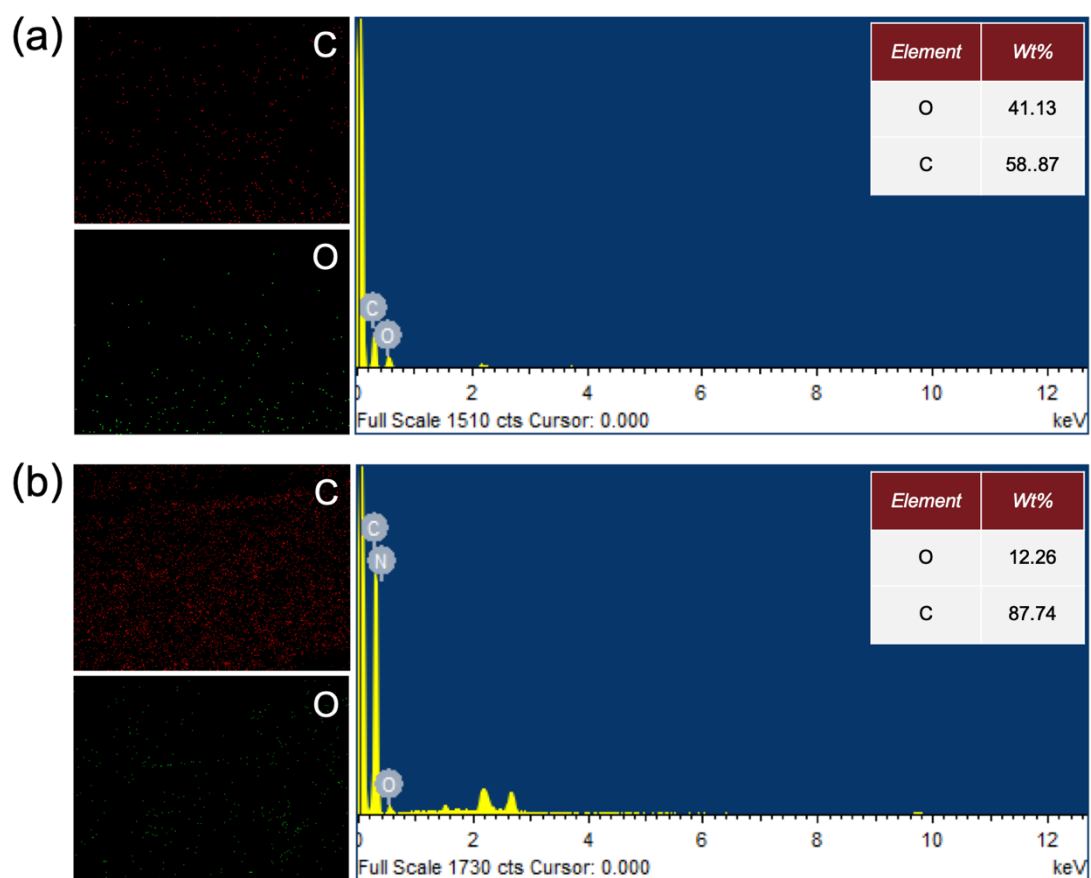


Figure 103 The EDS analysis and mapping results of each element of (a) pristine cotton fabric and (b) cotton-PANI/CNT 1.50 g.

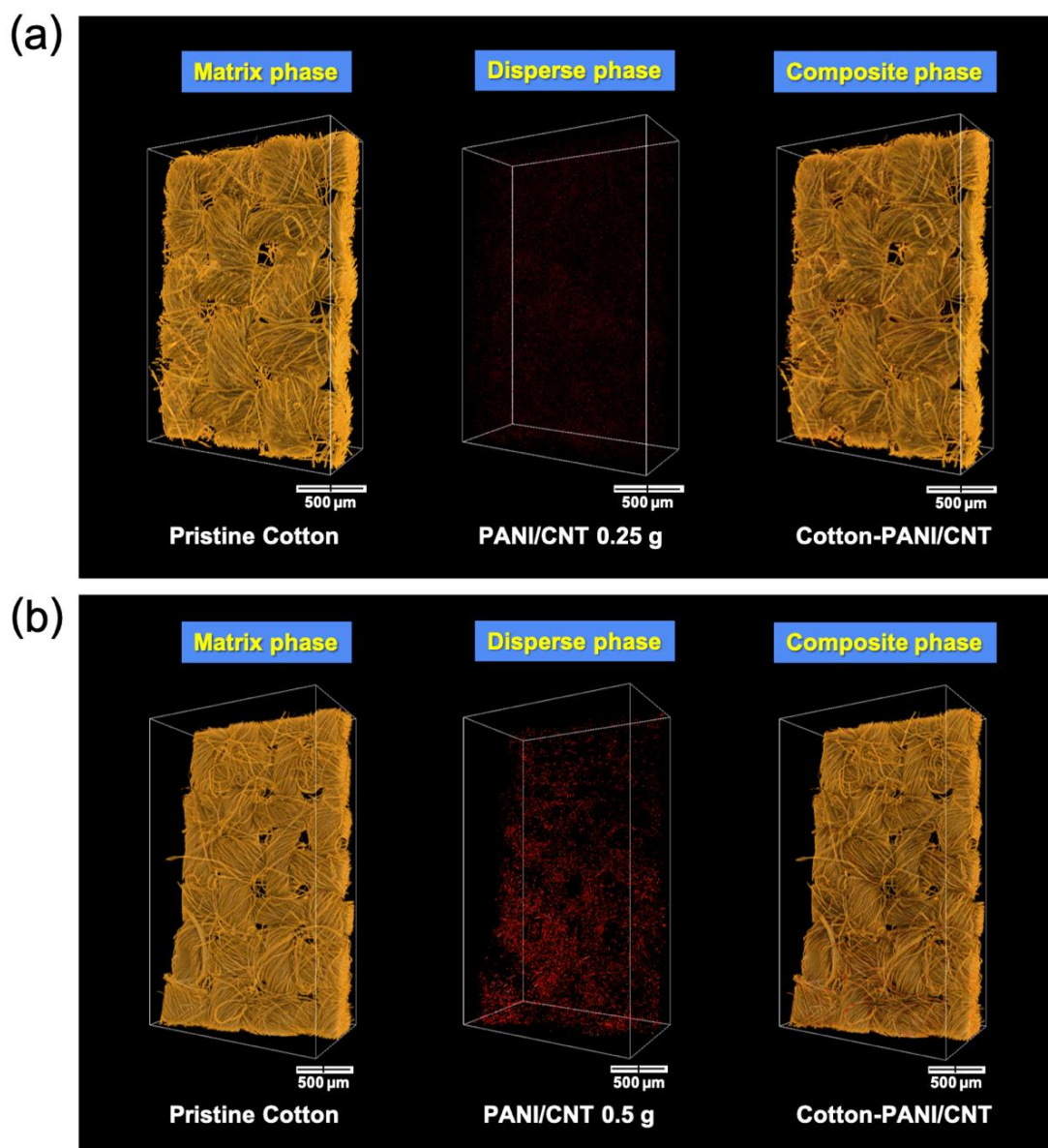


Figure 104 The SRXTM 3D visualization of cotton/PANI/CNT (a) 0.25 g and (b) 0.50 g

Furthermore, the 3D visualization of cotton/PANI/CNT was observed by SR-XTM. According to Figure 104a-b, the 3D images are separated into three phases including the structure of cotton fabric, the distribution of PANI/CNT and the composite phases of cotton/PANI/CNT fabric. The results demonstrate the matrix phase of cotton fabric within dark yellow color, where the fillers of PANI/CNT powder dispersive phase are indicated within red color. The dispersion of PANI/CNT 0.25 g (Figure 104a) is compared with PANI/CNT 0.5 g (Figure 104b). It can be seen that, an increase of PANI/CNT dispersion

correlates with an additional PANI/CNT content. Also, some agglomerates of powders have appeared, relating to the SEM results and EDS analysis. In addition, the filler of PANI/CNT is not only dispersing over the fabric areas, but also deeply incorporated inside the cotton structure and wrapped around the cellulose fibers. It can conclude that the cotton fabric is successfully composite as three phases' composites. By comparing the physical properties and morphology between cotton/PANI and cotton/PANI/CNT composite fabric, a flexibility and similarity in morphology was found. Furthermore, both of composite fabric's morphology show a large dispersion of PANI relation to an additional of PANI contents which confirm a successful of the composite between fabric and PANI conductive polymers.

#### 4.2.7.1 Chemical structure characterization of cotton fabric and cotton/PANI/CNT composite fabrics

For cotton/PANI/CNT system, the chemical structure characteristic of cotton and cotton/PANI/CNT fabric was examined by Raman technique. In Figure 105a, the expanding of Raman shift shows a clear detail of Raman spectra for pristine cotton at the range of 1000-1400  $\text{cm}^{-1}$ . The characteristic peaks of pristine cotton at 1096 and 1123  $\text{cm}^{-1}$  are attributed to the asymmetric and symmetric stretching vibration of C-O-C group. Also, the C-C stretching vibration and bending vibration of C-O-H and  $\text{CH}_2$  group were observed at 1153, 1250 and 1345  $\text{cm}^{-1}$ , respectively. According to the cotton fabric after dip-coated with various condition of PANI/CNT (0.05, 0.25 and 0.50 g), the Raman spectra was characterized in the region of 1000-3000  $\text{cm}^{-1}$  to observe all characteristics of cotton, PANI and CNT. As shown in Figure 105b, the characteristic peaks of PANI ascribe the bending vibration of C-H group at 1165  $\text{cm}^{-1}$  and C=N stretching vibration of 1486  $\text{cm}^{-1}$ . The results show that at a larger concentration of PANI/CNT content, the Raman intensity and the sharpness of the C=N stretching vibration peaks are also increased. Moreover, the cotton/PAN/CNT show the presence of the D- band and G- band and G'- which correspond to the CNT characteristic at 1342 and 1580  $\text{cm}^{-1}$ (107). The peak at 2680  $\text{cm}^{-1}$  attribute to overtone D-band or normally known as G'-band which

also related to the Raman scattering of CNT characteristic (39,92). Thus, in addition to morphology characteristics, all of the spectra by Raman technique are another way to confirm the successful preparation of cotton fabric composite with PANI/CNT powder.

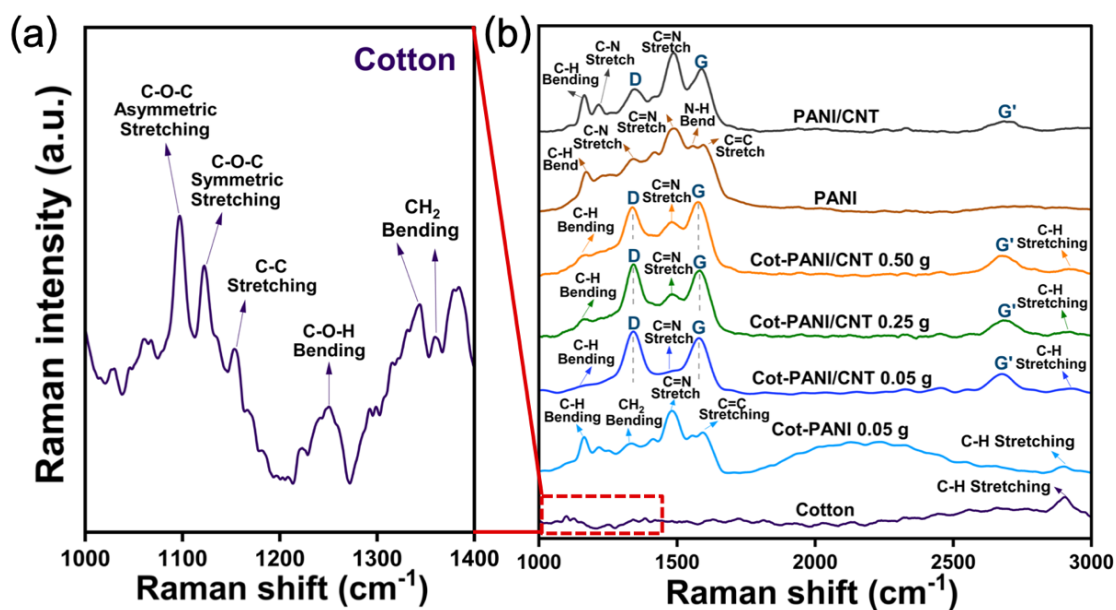


Figure 105 The Raman spectra of pristine cotton compared with cotton/PANI/CNT at various conditions

After the morphological and chemical structural characteristics of synthesized powder (PANI and PANI/CNT) and composite fabrics based on Rayon/PANI, cotton/PANI and cotton/PANI/CNT systems were characterized and confirmed. Consequently, the discussion of electrical properties, thermoelectric properties and output efficiency of hybrid TENG-TEG based cotton/PANI/CNT will be mentioned in the next section.

#### 4.2.8 The electrical properties, thermoelectric properties and output efficiency of cotton fabric and cotton/PANI/CNT composite fabrics

The electrical properties and thermoelectric properties of cotton fabric compared with cotton/PANI/CNT composite fabric was investigated by LCR meter and handheld digital multimeter. The explanation in this section focused on the thermoelectric and electrical properties, consisting of Seebeck coefficient ( $S$ ), power factor ( $PF$ ), impedance analysis, conductivity and resistivity. For the electrical output performance of both Rayon/PANI, cotton/PANI and cotton/PANI/CNT, the output of  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  were measured by using an oscilloscope and a DMM. Furthermore, the working mechanism within sliding mode of hybrid TENG-TEG device was explained to support the electrical output performance results.

##### 4.2.8.1 The electrical properties of cotton fabric and cotton/PANI/CNT composite fabrics

The electrical properties of cotton/ PANI/CNT composite fabric were investigated by LCR meter and handheld digital multimeter. The explanation in this section focused on impedance analysis, conductivity and resistivity. As seen in Figure 106, the impedance analysis was indicated in a Nyquist plot (71). The plot introduces the function of the imaginary part of impedance ( $Z''$ ) and the real part of impedance ( $Z'$ ). The semi-loop of impedance exhibits the resistivity of cotton fabric and cotton/PANI/CNT for all conditions (0.05, 0.25, 0.50, 0.75, 1.00 and 1.50 g). The results show that the loops present a difference of diameter which corresponds to the difference resistivity. At high frequency, the largest loop trend towards to the cotton/PANI/CNT 0.05 g (Blue line), followed by cotton/PANI/CNT 0, 0.25 and 0.50 g. For more detail of remaining conditions, the plot was expanded at low frequency and can be seen that the pristine cotton fabric demonstrates the largest loop, where the cotton/PANI/CNT 1.50 g (Red line) shows the smallest. The decrease in diameter of the loop relates to the decreasing of materials resistance (72,73).

Importantly, the evident loop can conclude that resistivity is decreased with an increase of PANI/CNT content. The cotton/PANI/CNT 1.50 g shows the lowest resistivity in this case. In addition, the  $Z$  of cotton/PANI/CNT 1.50 g at selected frequencies ( $10^2$ - $10^6$  Hz) with the function of temperature at room temperature (RT) to  $100^\circ\text{C}$ . In Figure 107, at room temperature, the  $Z$  of cotton/PANI/CNT 1.50 g reveals the highest value. While  $Z$  get decrease in lowest values at  $60^\circ\text{C}$ . It can conclude that the  $Z'$  values is not correlate to the rising temperature but depends on the working temperature of each thermoelectric materials (108). For this reason, the lowest  $Z'$  values are obtained at  $60^\circ\text{C}$ , which is the working temperature of PANI.

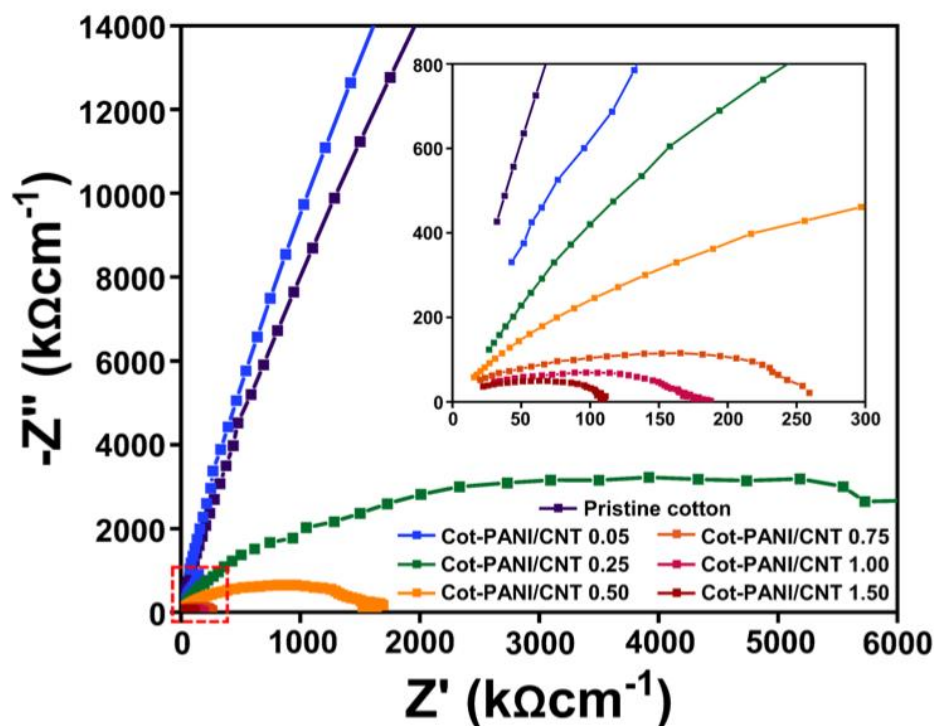


Figure 106 The impedance analysis illustrates the Nyquist plots in the function of the  $Z''$  impedance and the  $Z'$  impedance of cotton/PANI/CNT for all conditions.

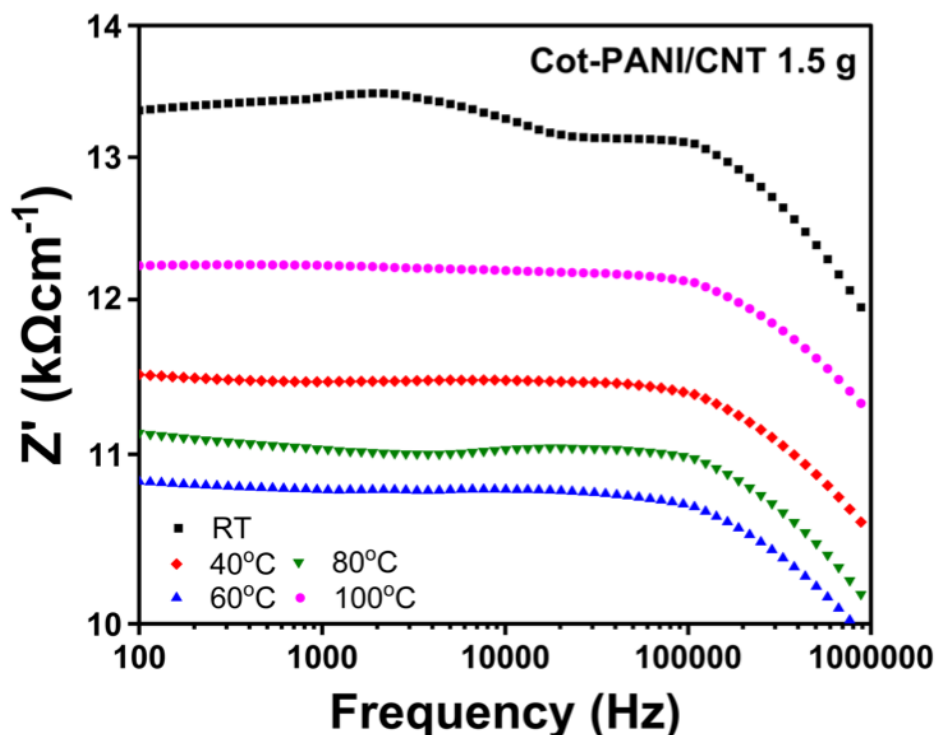


Figure 107 The impedance analysis illustrates the  $Z'$  impedance of cotton/PANI/CNT 1.50 g in the function of temperature.

Furthermore, the electrical conductivity was also measured as shown in Figure 108. The conductivity as a function of frequency ( $10^2$ - $10^6$  Hz) at RT of cotton/PANI/CNT fabric is reported. The results demonstrate that the conductivity significantly increases with the increasing of PANI/CNT content on cotton fabric. The pristine cotton indicated poor conductivity at a frequency of 1MHz. The cotton/PANI/CNT 1.50 g provided the highest conductivity of  $\sim 1.04 \text{ mS cm}^{-1}$ , followed by cotton/PANI/CNT 1.00, 0.75, 0.50, 0.25, 0.05 g. Furthermore, to confirm the working temperature of PANI, the conductivity at different temperature ( $T = \text{RT}-100^\circ\text{C}$ ) of cotton/PANI/CNT 1.50 g was analyzed as shown in Figure 109. The lowest conductivity was generated at RT, while reaching a peak at  $60^\circ\text{C}$ . This is evident that the conductivity values exhibited with the consistent trend of the impedance, relative to the varying of temperature. It was interesting that the temperature relating to the electrical properties of thermoelectric materials. According to the study, the PANI has the working temperature around  $\sim 40$ - $95^\circ\text{C}$  (109) which is an

important factor to generate an efficiency of electrical properties. It corresponding to the results that the best performance is demonstrate at 60°C. Notably, the electrical properties of the impedance and conductivity depend on the concentration of the charge carrier of thermoelectric materials. Containing the largest PANI/CNT content, leading the cotton/PANI/CNT 1.50 g has the highest charge carrier concentration that are the reason to reveal the best performance compared with other conditions. The other work of Tanty. N. *et.al*. Also, report with the same relation, the conductivity of PANI/CNT increased with an increase of PANI/CNT percentage. Conversely, the resistivity increased with a decreasing in percentage of PANI/CNT (92).

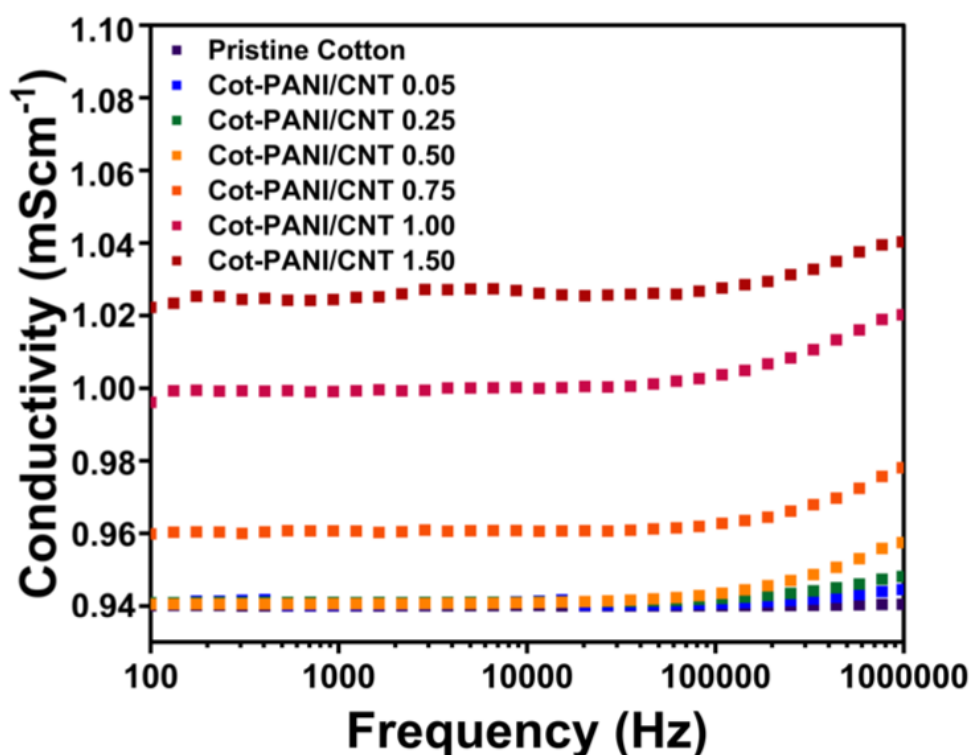


Figure 108 The electrical conductivity of cotton/PANI/CNT for all composition (0, 0.05, 0.25, 0.50, 0.75, 1.00 and 1.50 g).

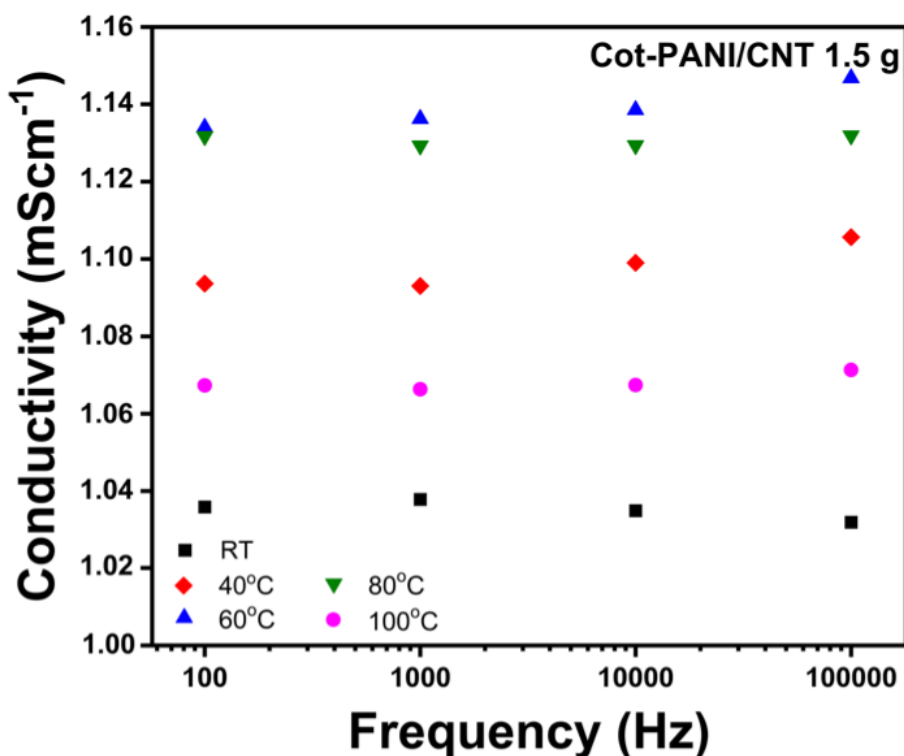


Figure 109 The electrical conductivity of cotton/PANI/CNT 1.50 g with a function of varying temperature

#### 4.2.8.2 The thermoelectric properties of cotton fabric and cotton/PANI/CNT composite fabrics

To support the electrical properties results, the thermoelectric properties were mentioned as shown in Figure 110-111. To examine the Seebeck coefficient of materials, it is essential to permit the conversion of thermal energy conversion to electricity. The coefficient relates to Equation 1. ( $S = \Delta V / \Delta T$ ) by measure the gradient of voltage ( $\Delta V$ ) with the responding of temperature gradient ( $\Delta T$ ) (55). First, the samples of pristine cotton and cotton/PANI/CNT with varying PANI/CNT (0.05, 0.25, 0.50, 0.75, 1.00 and 1.50 g) content were prepared. Each sample was attached with an electrode at both ends sides. The study of Zhang and co-worker procedure report the measuring-set up in laboratory scale (77). The measurement temperature was controlled on one side of the fabric samples by heat on the laboratory hot plate that act as the heat source, where  $T_{\text{hot}}$  was fixed at 60°C. Whereas, the opposite side of the

fabric samples were putted on the tray at RT to generated the  $\Delta T$  along the both side of the cotton-PANI/CNT composite (78). All of the samples were measured in the same way as explained above in a section of 4.1.3.2 When the heat energy was given to the system, the carriers then moved from heater side to the colder side. The mobility of the charge carriers generates thermo-voltage. The measurement of the  $\Delta V$  was recorded by the hand-held DMM and the  $S$  was calculated. At the same gradient of temperature, the  $S$  relative with a function of additional PANI/CNT content were analyzed, as seen in Figure 110. The  $S$  demonstrate a positive values, representing p-type thermoelectric materials of PANI/CNT that composite with pristine cotton fabric (110). This result exhibits that the relation of increase with the rising of the PANI/CNT content. For this reason, the maximum Seebeck coefficient value reached by cotton/PANI/CNT 1.50 g about 98.5 mV/K, which is  $\sim 7.8$  times larger than pristine cotton of 12.6 mV/K. Also, it demonstrates an increasing of PANI/CNT content derive to the increasing for concentration of charges carrier to more mobility, resulting in  $S$  large value.

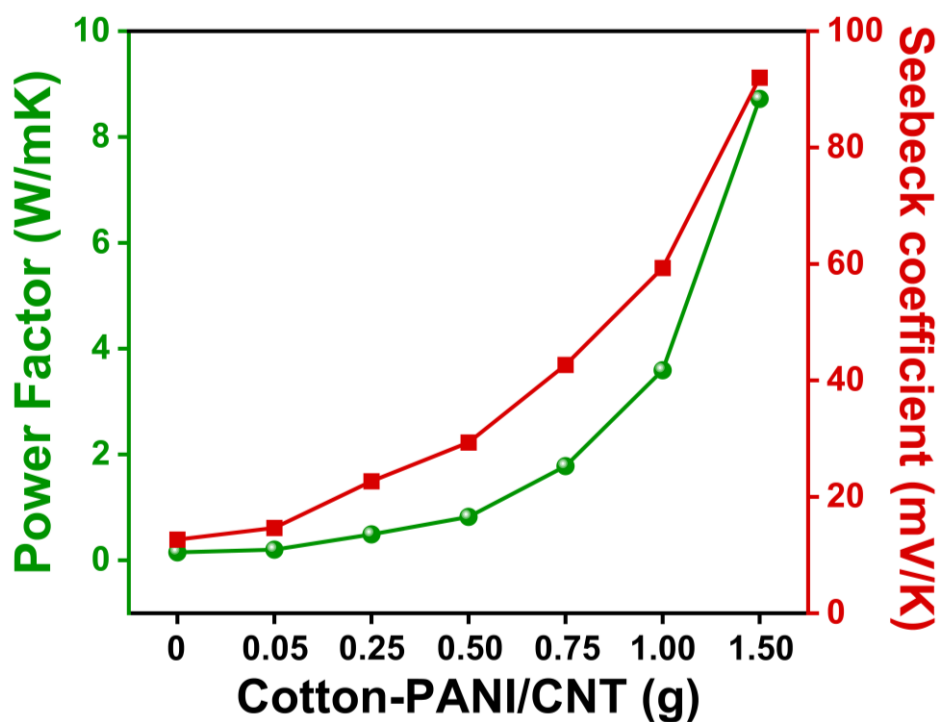


Figure 110 The Seebeck coefficient as a function of various PANI/CNT content compare with calculated power factor

To confirm the trend of  $S$  value, the calculation of power factor ( $PF$ ) was quantified to assess the thermoelectric performance, by Equation 4. The  $PF$  was plotted together with the  $S$  in Figure 110. The  $PF$  results demonstrate the relation between and as a function of various content of PANI/CNT. The results show the parallel trend of with, both thermoelectric properties dependence on the addition of PANI/CNT content. The cotton-PANI/CNT 1.50 g reaches a maximum value of 9 W/mK. This is correlated to the largest amount of PANI/CNT content. In addition, the as a function of different temperature from RT to 100°C was also calculated. It can show that the value is rising from RT to 60°C, while after that the value is gradually decreased as shown in Figure 111. The highest value reach at 60°C which relate to the working temperature of PANI (109,111).

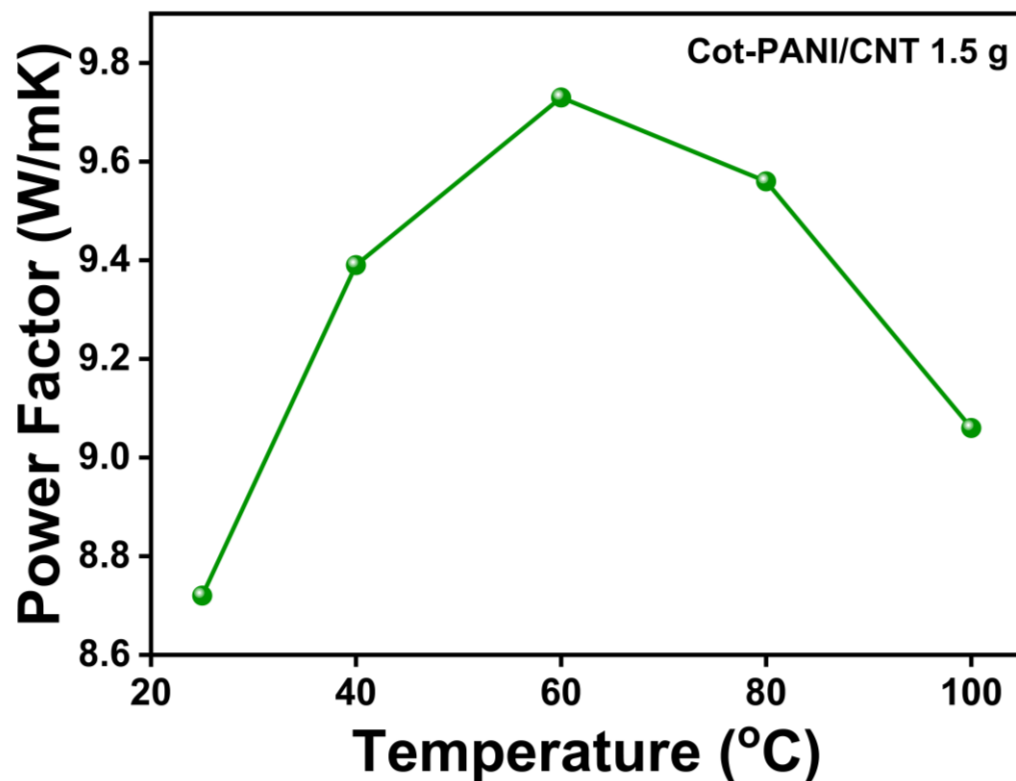


Figure 111 The calculated power factor with a function of various temperature

To confirm the performance of p-type thermoelectric materials of PANI/CNT, the junction effect was explained and measured by LCR meter. The junction graph represents the current density ( $J$ ) and voltage ( $V$ ) characteristic curves ( $J$ - $V$  curve) as a function of various cotton/PANI/CNT conditions (0.05, 0.25, 0.50, 0.75, 1.00 and 1.50 g). The samples were prepared like semiconductor p-type and n-type materials. The cotton fabric composite samples were collocated in different amounts of p-type PANI/CNT content pair with the reference n-type of cotton fabric/silver selenide ( $\text{Ag}_2\text{Se}$ ) thermoelectric materials. Usually, the  $J$ - $V$  curves are behaving in S-curve form to present the p-n junction effect. The S-curve consisting of zero bias, forward bias and backward bias region (83). In this work, the voltage in a range of -5 to 10 V was biased to generate the  $J$ - $V$  curve, as characterized in Figure 112. The results show the non-linearity in the curves which present in S-curve form, obviously present in the cotton/PANI/CNT 1.50 g condition, confirming the p-n junction of thermoelectric property of prepared fabric. The junction interface during sliding was found to play a crucial role in generating additional charges through the between thermoelectric and triboelectrification. It is also evident that the concentration of charge carrier expanded with the increasing of delocalize electrons, due to the rise of PANI/CNT content. While during the sliding motion working mechanism, the materials are junction together to generate the additional charges. Authenticating, the incorporation between thermoelectric and triboelectric effect.

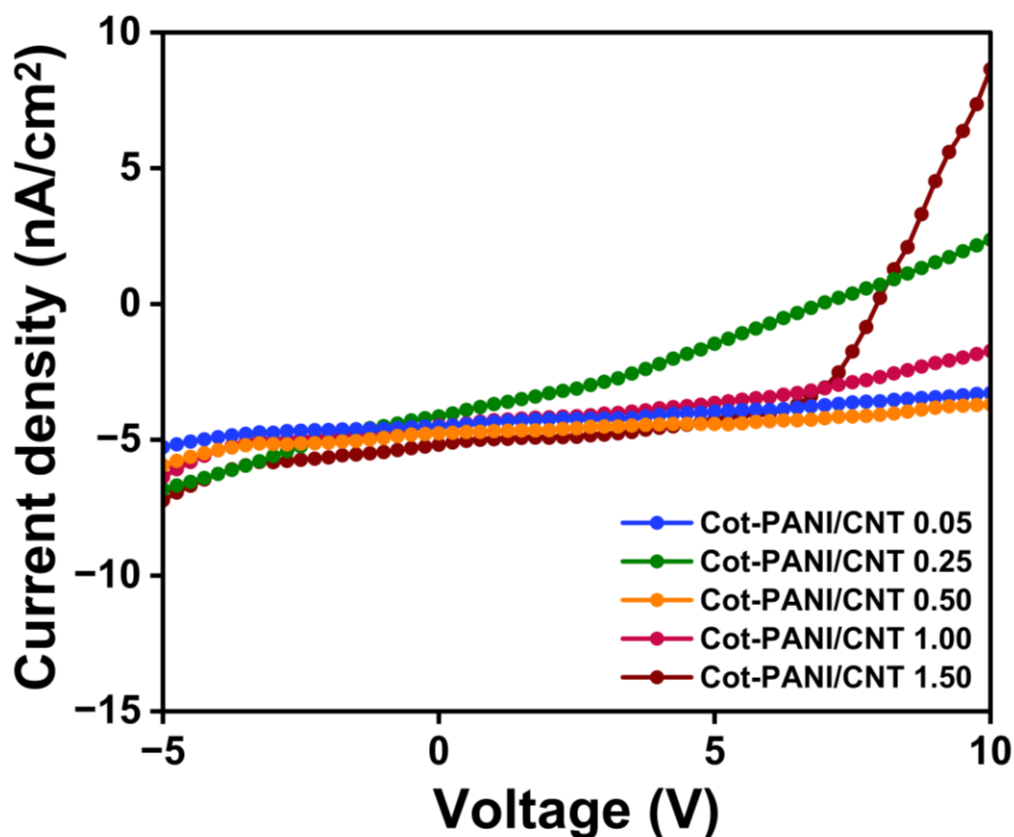


Figure 112 J-V characteristic curves with a function of various cotton/PANI/CNT

#### 4.2.9 The working mechanism and electrical output performance of cotton fabric and cotton/PANI/CNT composite fabrics hybrid TENG-TEG devices

For the electrical output performance of cotton/PANI/CNT, the output of  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  were measured by using an oscilloscope and a DMM. Furthermore, the working mechanism within sliding mode of hybrid TENG-TEG device was explained to support the electrical output performance results.

##### 4.2.9.1 The electrical working mechanism of cotton/PANI/CNT composite fabrics hybrid TENG-TEG devices

The working mechanism and structural of cotton/PANI/CNT hybrid TENG-TEG system demonstrate as same as the Rayon/PANI and cotton/PANI hybrid TENG-TEG system. The structure of device consists of two different tribo-

materials, where tribo-positively contact layer (upper part) is cotton fabric composite with PANI/CNT thermoelectric materials and Teflon film act as tribo-negatively contact layer. Both sides of tribo-materials attached with conductive fabric and Al tape, functioning as electrode. These two layers were placed along each other parallelly. The device was represented as cotton/PANI/CNT hybrid TENG-TEG within operation mechanism of LS-mode. The details of LS-mode TENG mechanism were explained in Figure 87. In the initial state, the two tribo-materials layers are pasted in parallel direction with full of contact, generating the triboelectric charges on each material surface. The cotton/PANI/CNT produces positive charges due to the electron donating ability, while the Teflon film exhibits the electron accepting behavior, creating negative charges. Meanwhile, the neutral without any charges transfer was demonstrated in this state owing to the creation of both charges equally. During the sliding motion was constructed, the upper layer of cotton/PANI/CNT start sliding outward until fully motion (state I-II). The unbalance of triboelectric charges of the layers occurred and induced the opposite charges to both electrodes. The Al tape bottom electrode generates positive charges, making the negative charges on conductive fabric (top electrode). A potential difference is then created and driven the electron to export throughout the external load, producing the signal of positive current. Consequently, the motion is ongoing slide inward (state III-IV) with a few of the layer's surface that remain connect, facilitating the continuous flow of charges. The charges from the top electrode move backward to the bottom electrode with achieving current in an opposite direction of the negative current signal (86). It results in an alternating current (AC) waveform caused by the repletely sliding mechanism. Here at this state, the continuous sliding motion not only generates electricity but also provides heat energy. Heat energy is another driving force of charges losing. In another case, it can also be mitigated by thermoelectric effect from the composite of PANI/CNT, multiplying the triboelectric charges. So, the charges could be generated within two effects, including the triboelectric effect and the heat conduction effect. The mechanical sliding motion between cotton/PANI/CNT fabric and Teflon film layer creates the charges performed by triboelectrification. Whereas the

conduction of heat energy facilitated by PANI/CNT also produced an additional of the charges. Thus, both effects from mechanical and thermal energy capability to promote an electrical output in the hybrid TENG-TEG system.

#### 4.2.9.2 The output efficiency of cotton/PANI/CNT composite fabrics TENG-TEG devices

First, the importance of temperature factor to the hybrid TENG-TEG system was studied with the electrical experiment was mentioned. Along the  $V_{oc}$  testing of cotton/PANI/CNT 1.50 g as a function of sliding time for 20 minutes (Figure 113a), the thermal camera is capturing the hybrid TENG-TEG device every 5 minutes. According to Figure 113a, as time passes, the results reveal an obvious increase of the  $V_{oc}$  from 0 V to 24.50 V and steady rise to 32.96 V. The growth of  $V_{oc}$  caused by an expanding of the temperature as seen in thermal images of hybrid TENG-TEG device in Figure 113b. The heat source creates at sliding zone and reach the peak temperature in a range of 40-50°C, corresponding to the working temperature of PANI/CNT thermoelectric materials. It can confirm that temperature is one of the factors relative to output performance.

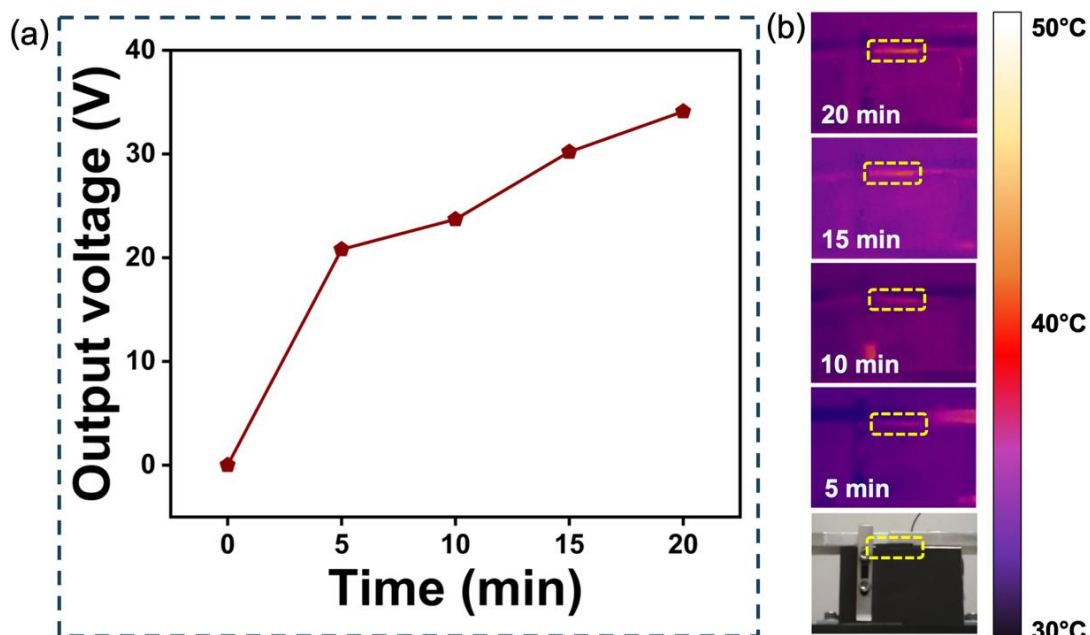


Figure 113 (a) The output voltage as a function of sliding time with (b) thermal images of the hybrid TENG-TEG device on the sliding machine

Consequently, the electrical output of hybrid TENG-TEG cotton/PANI/CNT with varying of PANI/CNT content (0, 0.05, 0.25, 0.50, 0.75, 1.00 and 1.50 g), was tested within two systems including unheated and heated system. According to Figure 114a-b, the electrical results of  $V_{oc}$  and  $I_{sc}$  were investigated at room temperature. The results demonstrate a significant increase of both  $V_{oc}$  and  $I_{sc}$  relative to a rise of PANI/CNT amount. Pristine cotton generates the  $V_{oc}$  of 11.18 V, followed by 15.52 V, 19.14 V, 24.60 V, 25.02 V and 25.74 V of cotton/PANI/CNT 0.05, 0.25, 0.50, 0.75 and 1.00 g, respectively. Whereas the cotton/PANI/CNT 1.50 g reaches the highest value of 32.96 V. Like the  $I_{sc}$ , the values increase in a similar direction. The cotton with varying PANI/CNT content achieved 13.31 mA, 15.57 mA, 19.85 mA, 27.31 mA, 29.55 mA, 32.40 mA and 50.09 mA. The highest  $V_{oc}$  and  $I_{sc}$  values given to the cotton/PANI/CNT with 1.50 g which is three times larger than pristine cotton.

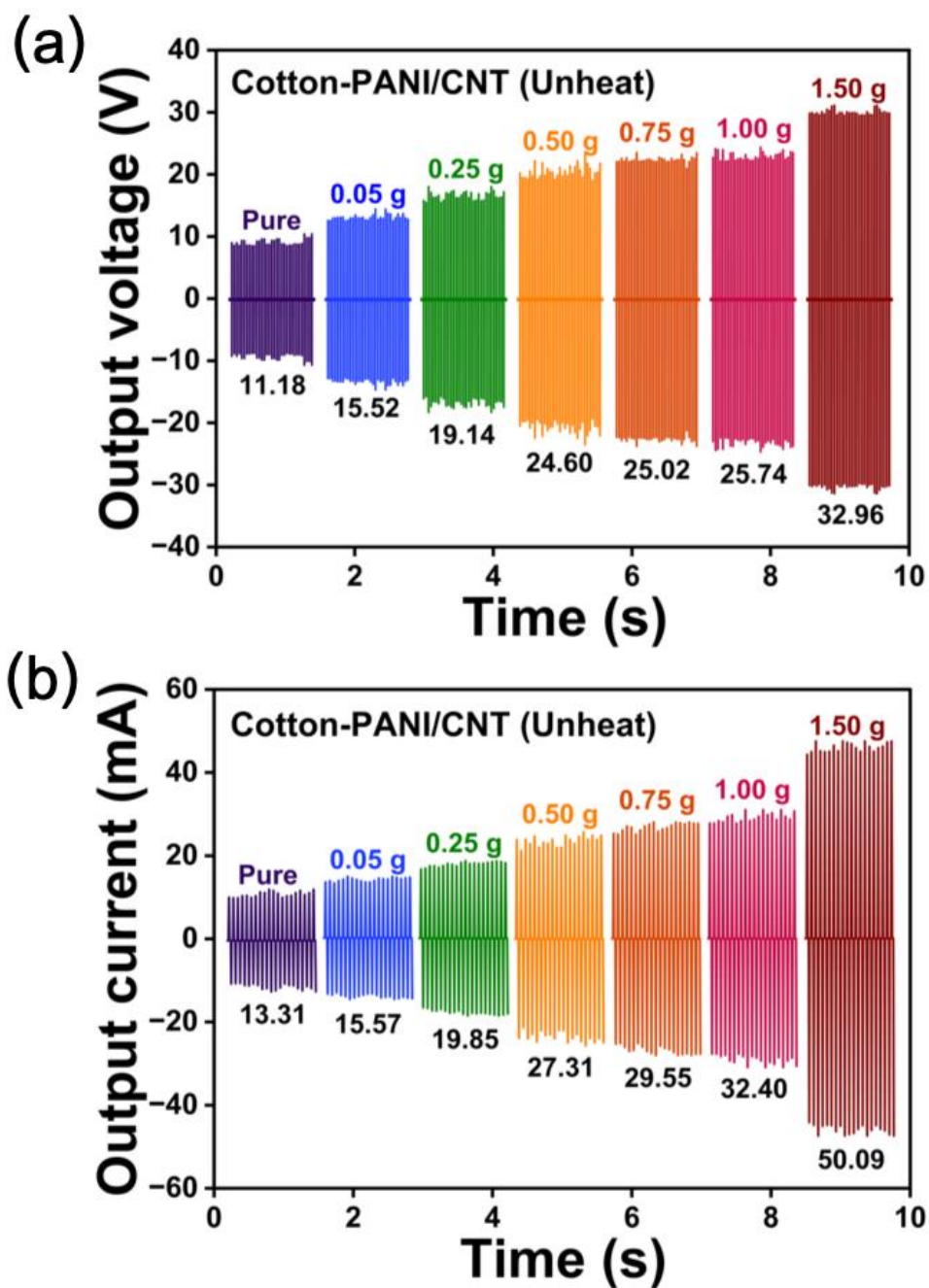


Figure 114 The electrical output performance in unheated system including (a)  $V_{OC}$  and (b)  $I_{SC}$  of cotton/PANI/CNT hybrid-TENG-TEG device with varying PANI/CNT content

According to the cotton/PANI/CNT hybrid TENG-TEG, the temperature is directly affecting the electrical output performance. The working temperature of PANI/CNT (40-60°C) at 60°C was chosen to heat up the hybrid TENG-TEG materials by hot air oven,

due to the highest performance in electrical properties as shown in Figure 108-109. According to heated system, the results revealed higher in the  $V_{oc}$  and  $I_{sc}$  with the same increasing trend correlate to an addition of PANI/CNT content, comparing to unheated system as exhibited in Figure 115a-b. Moreover, the pristine cotton fabric without PANI/CNT content demonstrates the  $V_{oc}$  and  $I_{sc}$  values of about 22.01 V and 30.73 mA, respectively. Whilst the cotton/PANI/CNT 1.50 g reaches the highest values at 39.96 V and 77.34 mA which possess the increasing values of 1.9 and 2.5 times higher compared to pristine cotton. Moreover, it also indicates that the heat source is a crucial factor, as evidenced by the electrical output performance in Figure 115a-b. The comparison of electrical output between unheated and heated conditions for pristine cotton is shown in Figure 116a-b. The  $V_{oc}$  and  $I_{sc}$  of heated cotton are higher than that of unheated system by 1.9 and 2.2 times. Meanwhile, the  $V_{oc}$  and  $I_{sc}$  of cotton/PANI/CNT at the same condition in the heated system demonstrate approximately 1.2 times and 1.5 times higher than that of unheated condition, as can be seen in Figure 117a-b. However, the output efficiency of cotton/PANI/CNT is larger than pristine cotton fabric in both systems unheated and heated system. As mentioned earlier, the unheated and heated conditions are basically set to prove the thermoelectric behavior. However, the thermoelectric behavior is not clearly presented because heat could play an important role to enhance the electrical output for both pristine cotton and cotton/PANI/CNT composite. The thermal energy can drive more charges to the load at a same time. Meanwhile, the addition of PANI/CNT can generate more concentration of charges carrier than that of using pristine cotton. This trend of result is similar to the results of Rayon/P3HT composite. The comment on this case is already provide in the part of Rayon/P3HT system.

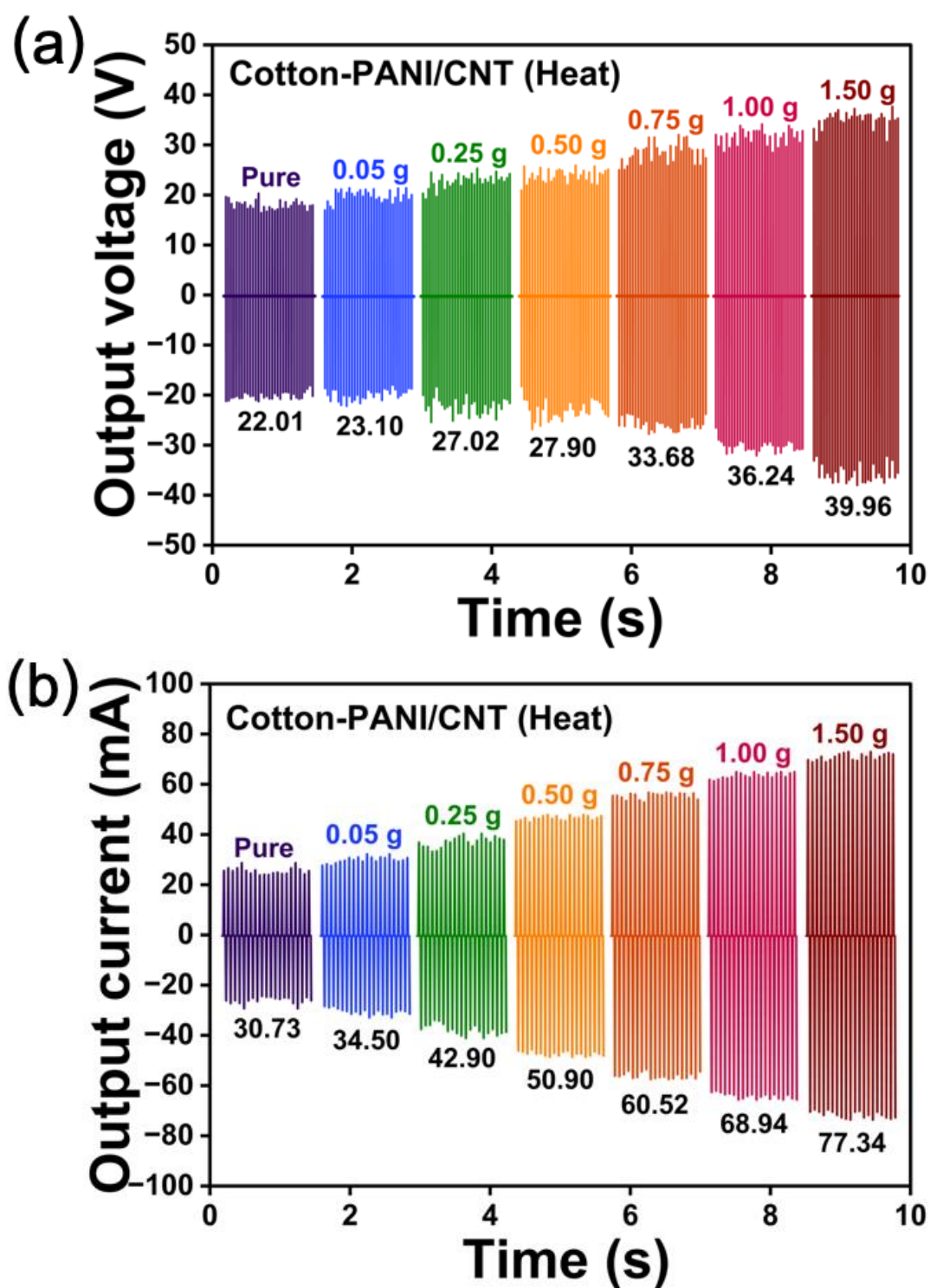


Figure 115 The electrical output performance in heated system including (a)  $V_{OC}$  and (b)  $I_{SC}$  of cotton/PANI/CNT hybrid-TENG-TEG device with varying PANI/CNT content

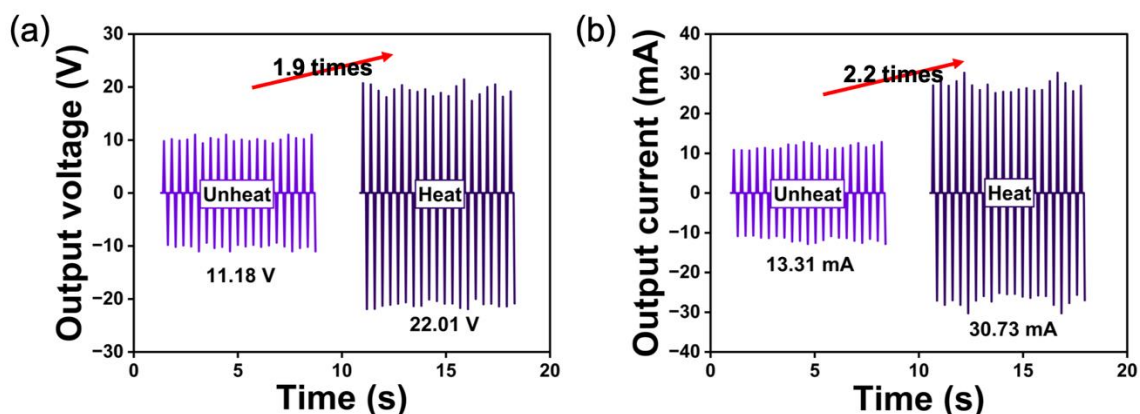


Figure 116 The comparison in terms of (a)  $V_{OC}$  and (b)  $I_{SC}$  within unheated and heated system of pristine cotton

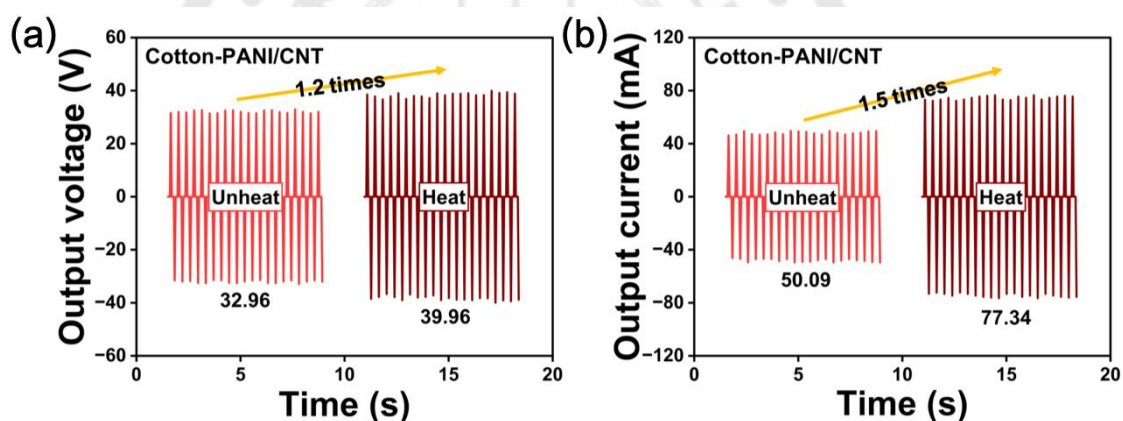


Figure 117 The comparison in terms of (a)  $V_{OC}$  and (b)  $I_{SC}$  within unheated and heated system of cotton/PANI/CNT hybrid TENG-TEG device at 1.50 g of PANI/CNT content

Furthermore, frequency is also an important point. The  $V_{OC}$  and  $I_{SC}$  with an input mechanical energy of the variation frequency between 2 to 10 Hz were measured as exhibit in Figure 118. At the lowest frequency of 2 Hz, the  $V_{OC}$  and  $I_{SC}$  of cotton/PANI/CNT 1.50 g provide ~4.80 V and ~22.75 mA, respectively. As the frequency increased to 6 Hz, the  $V_{OC}$  and  $I_{SC}$  were generated higher about 13.77 V and 44.90 mA. Whereas the frequency continuously rises to 10 Hz, the output performance was expanded to approximately 39.96 V and 77.34 mA which is higher values than obtained

at low frequencies. As the frequency has increased, mechanical energy also incorporates along with the heat energy. Therefore, the large electrical output was performed at higher frequencies. Furthermore, as the results also demonstrate, the cotton/PANI/CNT with heat source gain higher  $V_{OC}$  and  $I_{SC}$ , confirming that the additional heat source incorporated with the mechanical energy can improve the electrical performance. All of the results evident that the hybrid TENG-TEG device capability to enhance the electrical properties and the output performance especially the output current by combining the mechanical energy with heat source. A comparison of electrical output improvement of previously cotton-based TENG with variation system is supported the results in Table 11. Additionally, a specific working temperature and the addition of PANI/CNT amount are an essential factor due to the enlarge concentration of charge carriers, affecting the electrical properties and output performance.

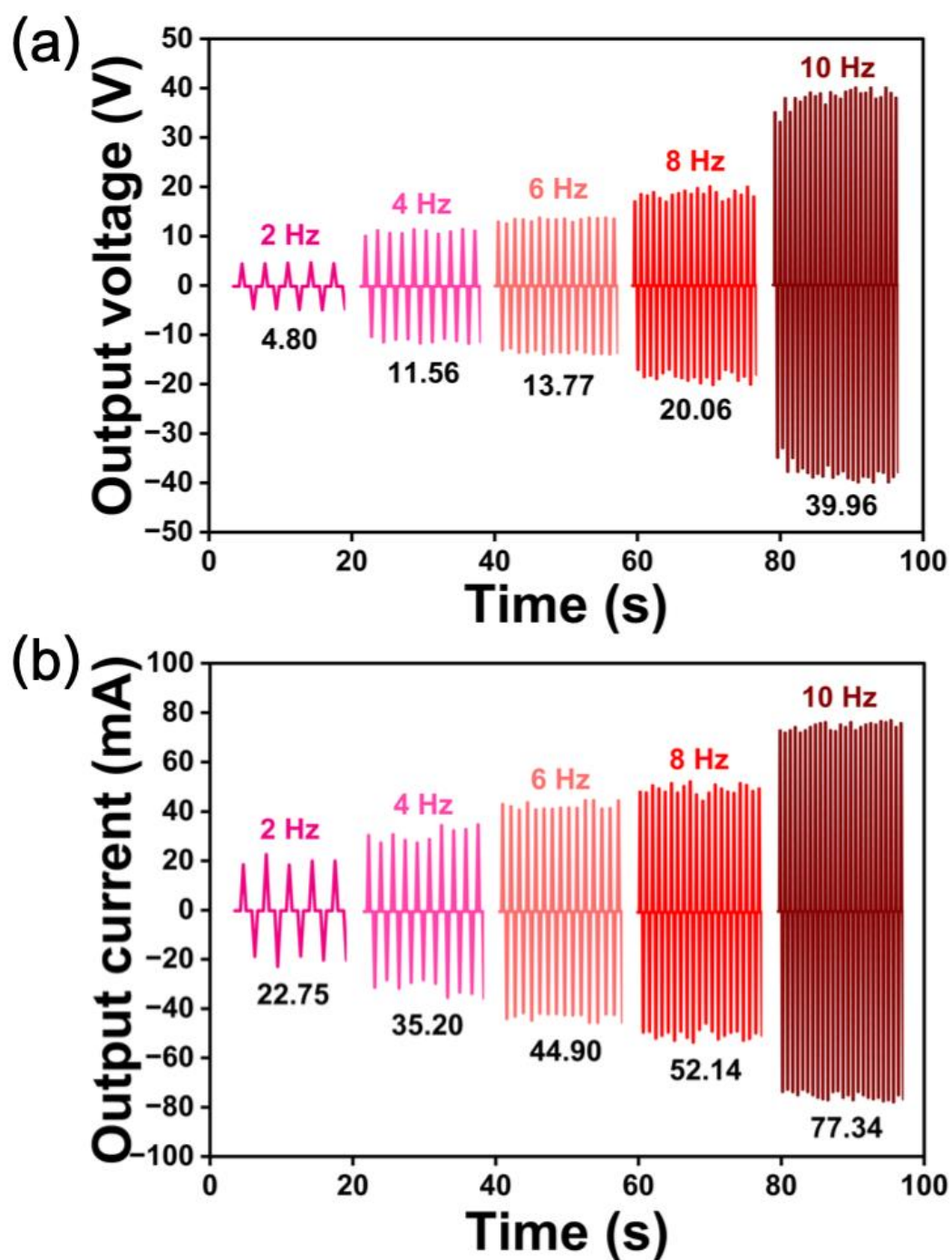


Figure 118 (a)  $V_{oc}$  and (b)  $I_{sc}$  of cotton/PANI/CNT 1.50 g at different frequencies ranging from 2-10 Hz

Table 11 The comparison of cotton-based TENG with variation system of previously work

| Materials              | System    | $V_{OC}$ (V) | $I_{SC}$ ( $\mu A$ ) | Power density<br>( $mW/m^2$ ) | Ref      |
|------------------------|-----------|--------------|----------------------|-------------------------------|----------|
| F-Cotton               | TENG      | 217          | 50.30                | 3,450                         | (14)     |
| Pristine cotton        | TENG      | 12.7         | 9.5                  | 97                            | (87)     |
| Cotton/PANI            | TENG      | 12.5         | -                    | -                             | (113)    |
| Cotton/CO              | TENG      | 350          | 45                   | 11,250                        | (54)     |
| Cotton yarn/PA yarn    | TENG      | 420          | 54                   | 13,500                        | (114)    |
| Cotton/PTFE            | TENG      | 51           | 0.152                | -                             | (115)    |
| Cotton/PDOT:PSS        | TENG      | 145          | 3.3                  | 343.2                         | (116)    |
| 2/1 twill weave cotton | TENG      | 196          | 4.5                  | 110                           | (117)    |
| Mercerized cotton      | TENG-PENG | 1.77         | 0.1                  | 9                             | (118)    |
| SF-cotton              | TENG      | 2500         | 85                   | 29,000                        | (119)    |
| Cotton/PANI            | Hybrid    | 34           | 47                   | 567.5                         | Our work |
|                        | TENG-TEG  |              |                      |                               |          |
| Cotton/PANI/CNT        | Hybrid    | 39.96        | 77,340 $\mu A$       | 876.7                         |          |
|                        | TENG-TEG  |              | 77.34 mA             |                               |          |

To supplement the enhancing of the output performances, the  $P_{max}$  of pristine cotton and cotton/PANI/CNT was investigated under the external load resistance of  $1k\Omega$  -  $10M\Omega$ . Based on Ohm's law:  $V=IR$ , the relationship between output voltage, output current and output power was shown. The results show the rising of output voltage with the increasing of external load resistance while the output current is drop (88). According to Figure 119a, the  $P_{max}$  of pristine cotton fabric reveal approximately  $49.6 \mu W$  based on the external load resistance of  $1M\Omega$ , whereas the  $P_{max}$  of  $263 \mu W$  was generated by cotton/PANI/CNT 1.50 g, as shown in Figure 119b. It demonstrates a higher value than that of pristine cotton by 5.3 times, due to composite of PANI/CNT, as

depicted in Figure 119a-b. The results also show that each sample has a specific external load resistance which correspond to an internal resistance, receiving the  $P_{max}$ . Whereas pristine cotton fabric and cotton/PANI/CNT 1.50 g have a specific resistance of  $1M\Omega$ . It can conclude that both temperature and the number of PANI/CNT compositions associate to the charge carrier concentration, resulting the cotton/PANI/CNT 1.50 g to generate highest output performance of  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  in this system.



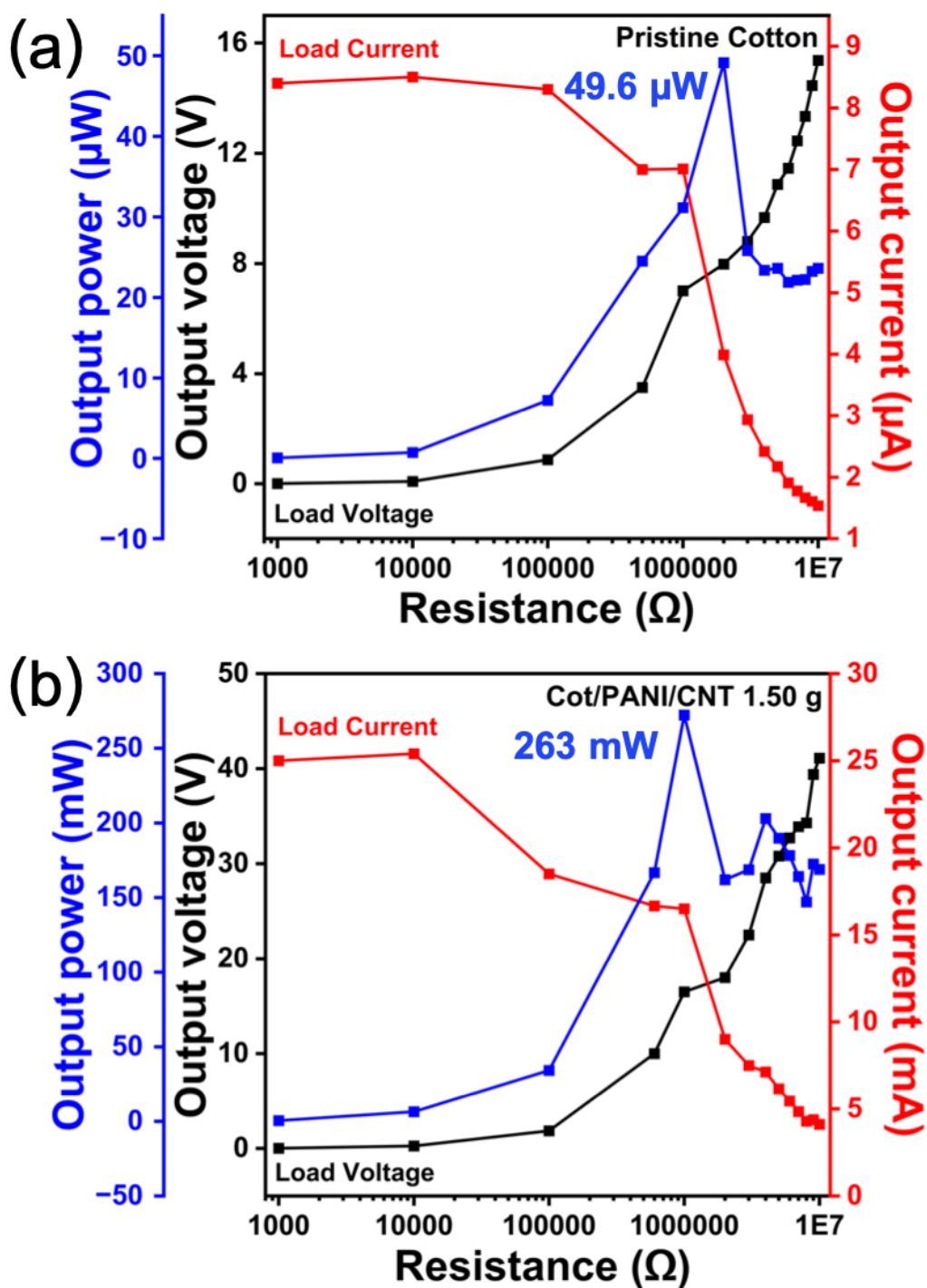


Figure 119 Maximum output power of (a) pristine cotton and (b) cotton/PANI/CNT 1.50 g under the resistance of  $1\text{k}\Omega$  -  $10\text{M}\Omega$ .

In addition, to test the stability used in longer period of time, the output voltage stability waveform of cotton/PANI/CNT 1.50 g was revealed in Figure 120. It exhibits a slight change of voltage waveform over a duration time of 2000 sec. The waveform also expanded and seen the characteristic of AC voltage, achieving the positive voltage signal and negative voltage signal of 39.96 V and -39.96 V. The results confirm that, even if the hybrid device is working longer, the voltage signal is still the same, presenting the stability of the device to use in real application. Also, to test the ability of hybrid TENG-TEG device in this work for apply in real application, the chargeability of cotton/PANI/CNT 1.50 g was measured by connecting with bridge diode. The chargeability as a function of various capacitor of 0.22  $\mu\text{F}$ , 0.33  $\mu\text{F}$ , 2.2  $\mu\text{F}$  and 3.3  $\mu\text{F}$  was represented in Figure 121. The capacitance of 0.22  $\mu\text{F}$  values demonstrate a chargeability that reach a maximum voltage about 15.9 V within 10 sec. In contrast, the other capacitance values are unaccomplished charging within 10 sec. However, the 0.22  $\mu\text{F}$  capacitance values indicate an ability to serve as power supply source for driven small electronic devices.

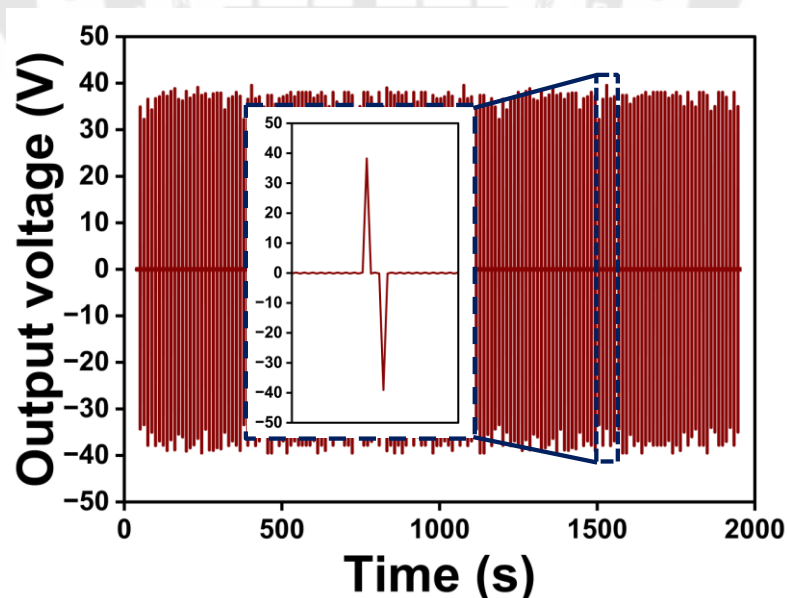


Figure 120 The output voltage stability waveform of cotton/PANI/CNT as a function of times within 2000 sec.

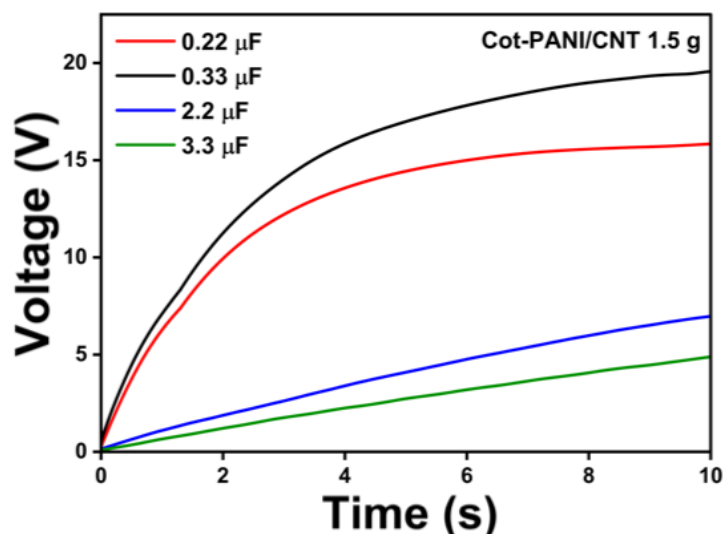


Figure 121 The chargeability of cotton/PANI/CNT 1.50 g with various capacitors

To verify the ability to drive a small electronic device, the cotton/PANI/CNT 1.50 g illustrates the capability to completely light up above 100 LEDs in parallel circuit connection. Also, an advancement to drives the LEDs by connecting into “SWU” alphabet within both parallel and series circuit connection was depicted in Figure 122a. It exhibits completely illuminated which confirms the potential of cotton/PANI/CNT composite fabric. Moreover, the driving of digital watch (Figure 122b) and the safety flashing light for bicycle or outdoor activities (Figure 122c) was also tested by connecting the circuit with capacitor and diode bridge to convert alternating current (AC) to direct current (DC), as shown in Figure 122b-c. The other recent work of cotton-based TENG device also reports the output performance with a use of application, as concluded in Table 12. In conclusion, the cotton-PANI/CNT 1.50 g reported flexibility and sufficient efficiency to boost small electronic devices, making it suitable to utilize and integrate into wearable devices for promote the wearable systems from now on.

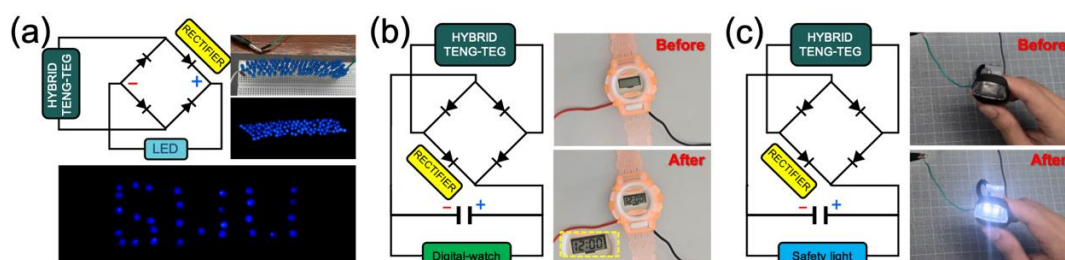


Figure 122 The testing of (a) driven LEDs, (b) digital watch and (c) safety flashing light

Table 12 The output efficiency and application of cotton-based TENG

| Materials       | Application                                              | $V_{OC}$ (V) | $I_{SC}$ ( $\mu A$ )       | Power density<br>( $mW/m^2$ ) | Ref      |
|-----------------|----------------------------------------------------------|--------------|----------------------------|-------------------------------|----------|
| F-Cotton        | 100 LEDs driven                                          | 217          | 50.30                      | 3,450                         | (14)     |
| Cotton/PANI     | Driving digital clock                                    | 12.5         | -                          | -                             | (113)    |
| Cotton/CO       | self-powered Fosbury flop sensor                         | 350          | 45                         | 11,250                        | (54)     |
| Cotton/PTFE     | self-powered sensors for fire alarm systems              | 51           | 0.152                      | -                             | (115)    |
| Cotton/PDOT:PSS | Self-powered sock                                        | 145          | 3.3                        | 343.2                         | (116)    |
| Cotton/PANI     | 90 LEDs                                                  | 34           | 47                         | 570                           |          |
| Cotton/PANI/CNT | 100 LEDs, digital watch and safety flashing light driven | 39.96        | 77,340 $\mu A$<br>77.34 mA | 2922                          | Our work |

### 4.3 The effects of conductive polymers on the electrical properties and output performance

All of the results of electrical properties and output performance show the relationship with the conductive polymers including P3HT, PANI and PANI/CNT composite. This enhancement corresponds to the conformation and arrangement along the polymer chain of PANI/CNT, which depend on thermoelectric effect of conductive polymers. P3HT is one of p-type conjugate polymers correlate to an alternating of sigma ( $\sigma$ ) bond and pi ( $\pi$ ) bond in molecular structure. They consist of thiophene ring with short hexyl group at side chains (120), as constructed in Figure 123. According to thiophene ring, the  $\pi$ - $\pi$  interactions occurred, locating the delocalized electrons. Whereas PANI is one of a semi-crystalline conductive polymers which is also known as conjugate polymer, correspond to an alternating of sigma ( $\sigma$ ) bond and pi ( $\pi$ ) bond in molecular structure that allowing polaron to delocalize along p-orbital. Herein, the PANI/CNT composite in this work is synthesized via in-situ polymerization by dispersing CNT and aniline monomers. The presence of an acid dopant of HCl was utilized in this study per the polymerization section. The PANI chains were directly grown along the CNT's surface to form the ordered packing chain formation within the Emeraldine base (EB) PANI structure. Consisting of alternating reduced (amine; -NH-) and  $\pi$ - $\pi$  interactions oxidized (imine; =N-) repeat units (121), as seen in a molecular structure of Figure 124. Consequently, the oxidized PANI is protonated to rearrange as conductive Emeraldine salt (ES) structure (90,122). The orbital exhibits the  $sp^2$  hybridization, consisting of benzene and quinoid rings interconnected by N atoms with  $\pi$ - $\pi$  bonds separated by a single bond. Focusing, the delocalize positively charged with lone pair electrons locate at the N atoms of the amine group (123), as demonstrate in Figure 125.

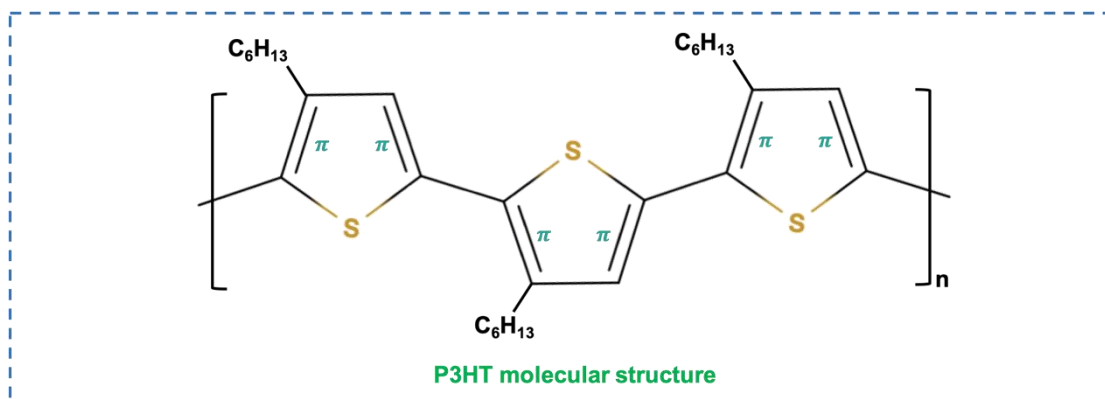


Figure 123 Schematic diagram of P3HT molecular structure.

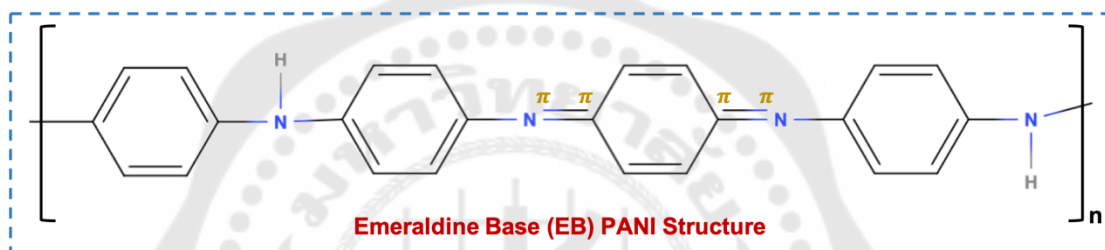


Figure 124 Schematic diagram of Emeraldine Base (EB) PANI molecular structure.

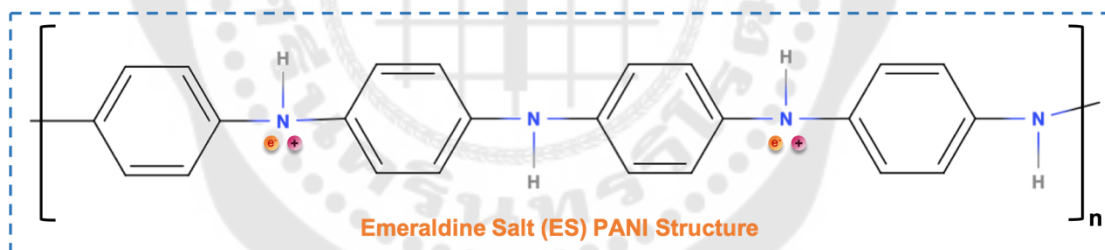


Figure 125 Schematic diagram of Emeraldine Salt (ES) PANI molecular structure.

As the operation of hybrid TENG-TEG device, the mechanical energy is given by sliding motion repeatedly, the heat energy also generated along with mechanical energy and serve as the driving force in the system. While heat source is applied to the system, it has enough energy to promote the transportation of charge carriers. The electrons can more easily move and transpose along the molecular backbone of P3HT and PANI conductive polymers by hopping process, Causing the generation of holes carrier through the structure of P3HT and PANI, as depicted in Figure 126 and 127, respectively. The charges then export to the external load, leading to generate the

electrical conductivity and electrical output efficiency. According to the composite, the CNT was incorporated alongside the PANI monomers. The interaction part contains the  $\pi$ - $\pi$  bonds represent the crystalline part of the PANI, obtaining the delocalized electron with high charge mobility. While the amorphous part consists of amorphous chain stacking together which composed of low charge mobility, leading to store the localized electron that are poorly conductivity (124,125). The CNT contributes to increased charge mobility, building the carriers easily to transfer through the structure. As illustrate in Figure 128, while the driving force of heat are sufficient, the lone pair electron of PANI can move along the molecular backbone through the CNT and export to the external load, promoting the conductivity and electrical output in a series circuit.

The electronic structure of p-type conductive polymers was also discussed to support the electrical mechanism. When sufficient heat source was produced to the system, the flowing of charges carrier occurred as described above. The delocalized-positively charges (polaron) and delocalized-negatively charges (electron) are hopping from electrons filled band (HOMO-level) to a higher-level, leading the energy band to decrease. Making the charges carriers easily hopped to an empty band (LUMO-level). It could be seen that the charges with sufficient energy capability to hop to the LUMO-level while the lower energy are localized. This behavior exists in form of known as polarons (60). Whereas in composite with CNT system, the charges containing in LUMO-level then transfer to the CNT structure and generated the electricity, corresponding to the thermoelectric mechanism, as seen in Figure 129 (60). As the number of PANI increased, the rise in charges concentration is also related to an easily transfer of charges due to the presence of CNT. This results in an improvement of thermoelectric properties, electrical properties and high output efficiency.

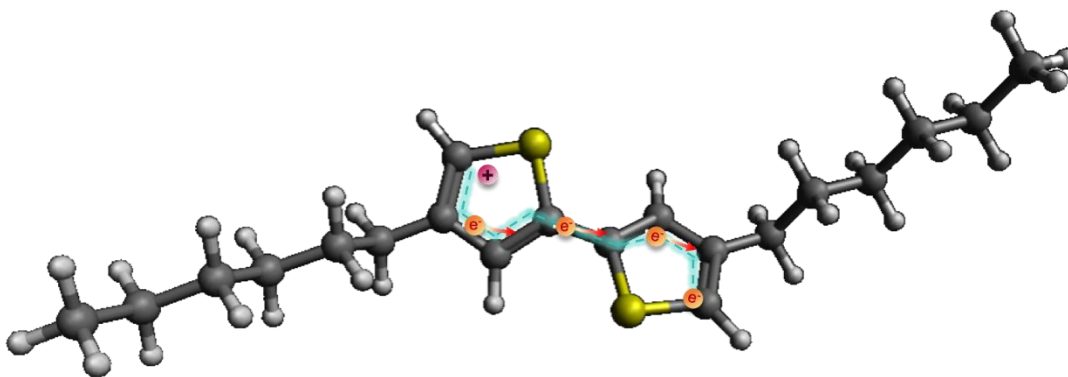


Figure 126 The illustration of 3D structure of P3HT with electron transportation.

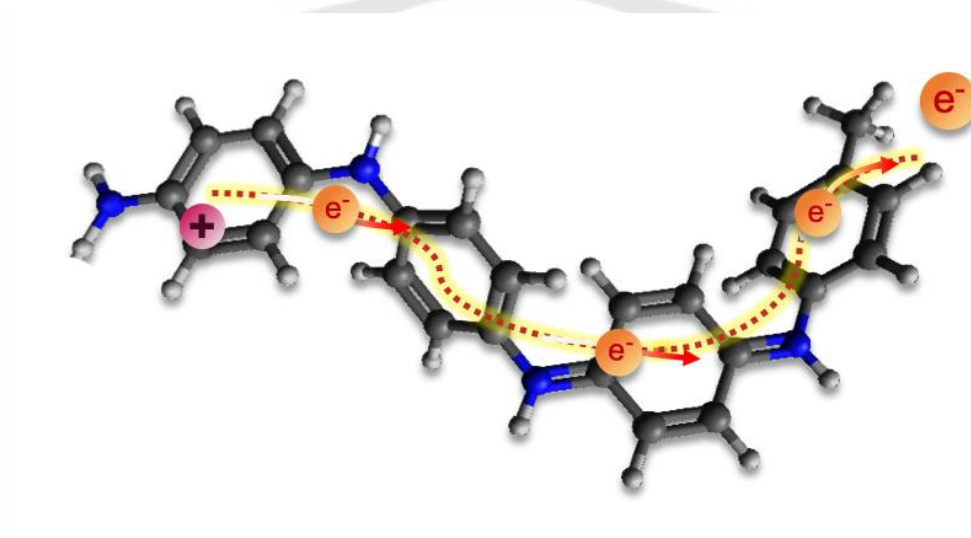


Figure 127 The illustration of 3D structure of PANI/CNT with electron transportation.

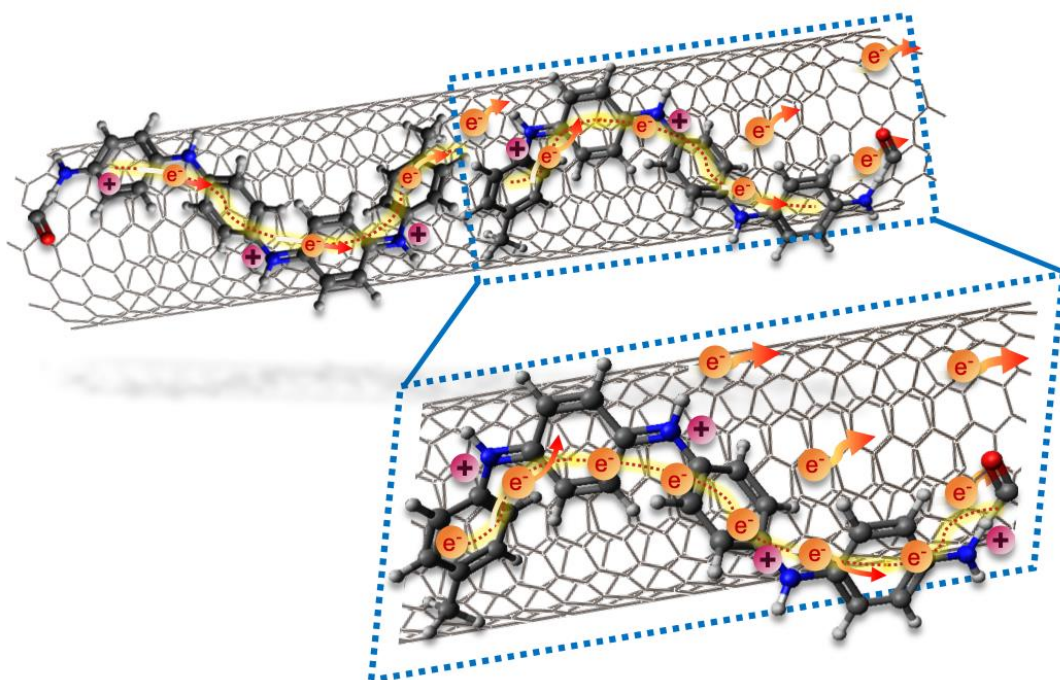


Figure 128 The illustration of 3D structure of PANI/CNT with electron transportation

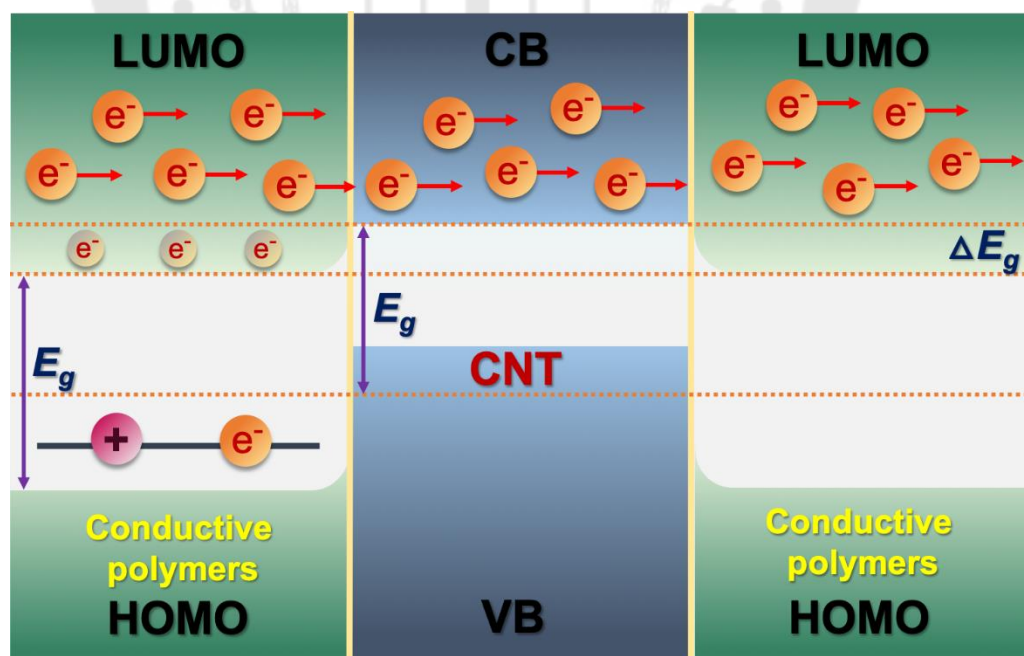


Figure 129 Electronic structure of conductive polymers/CNT composite powder

Normally, in the composite systems, the best electrical output performance of each system corresponds to the addition of conductive polymers until reaching the percolation threshold. The percolation threshold is the point of exact amount of filler phase to the matrix phase that the composite properties instantly change and reach maximum performance (126,127). In general, the percolation thresholds point are explained to achieving the best electrical properties, mechanical properties and also rheological properties (128). The attention of this work is given to the percolation threshold of conductive polymers to the electrical properties. According to J. Li and J. Kim's work, the explanation of percolation theory with electrical behavior was reported in power-law relationship, according to Equation 5. The electrical conductivity of composite and the filler are presented in  $\sigma$  and  $\sigma_0$ . Whereas  $V_f$  is the filler volume fraction, the percolation threshold are  $V_c$ , and  $s$  is a conductivity exponent (129).

$$\sigma = \sigma_0(V_f - V_c)^s$$

Equation 5 power-law relationship

According to an Equation 5, while the  $(V_f - V_c)$  increased, the electrical conductivity of composite increased. There are a variety of works that studied about percolation threshold in composite system. The work of H. J. Choi et.al. prepared the composite between carbon black (CB) and different types of polymers. They reported that the different type of polymer matrix represents the contrast critical amount of CB which show the different percolation threshold behavior. Also, the different percolation threshold amount of CB/polymers composite exhibited the different electrical conductivity owing to the polarity and crystallinity of each matrix, which corresponds to Equation 5 (130). S. Ukasi et.al. discussed that the percolation system or known as the critical point is relative to the distribution of filler particles to the matrix phase. When the filler was added to the matrix phase at a certain amount, the particles are attached

together and form the network, letting the charge can flow throughout the matrix phase (126).

In the case of cellulose-based fabric/conductive polymers in this work, the percolation threshold phenomenon was also studied. However, each system obtained different percolation point with different amounts of conductive polymers, owing to the dissimilar types of cellulose-based fabric's matrix phase. Starting with the results of the Rayon/P3HT composite fabrics, the better electrical properties and higher output signal were obtained by adding P3HT and reach the highest output values at 150 mg of condition. Here in this system, the percolation points have not been established because adding more than 150 mg could not be prepared. According to literature, J. Morita et.al reported the percolation point at 10 wt% of P3HT incorporating with other polymer matrix (131). Therefore, if the P3HT content can be increased more in this work, it would probably be able to find the percolation threshold. However, the P3HT could not be added higher than that of 150 mg to Rayon fabric because of some limitation as mentioned in the part of Rayon/P3HT preparation.

The other systems of Rayon/PANI and cotton/PANI represent the percolation point that only one condition can provide the highest electrical output. According to Rayon/PANI composite fabric, the maximum value of electrical output could be reached by adding the PANI for 0.25 g. This point related to the suitable amount of filler for nice distribution at  $0 < p_c < 1$ , where  $p_c$  is the amount of filler at percolation point (126). When the number of fillers is larger than the  $p_c$ , the agglomeration is represented. So, in this work, the increasing of PANI content more than 0.25 g led to the dropping of electrical output. It can conclude that the PANI 0.25 g represents the percolation threshold point which also presents the best distribution. Similarly, the cotton/PANI composite fabric also represents the critical point at 0.15 g, higher amount of PANI than 0.15 g conditions, the electrical output is decreased.

The electrical output efficiency relative to the percolation point can be schematically depicted in Figure 130. The addition of filler at lower content than  $p_c$  shows an uneven distribution which represents low electrical output efficiency, as shown

in state I. According to the filler's amount at percolation threshold, it presents the appropriate distribution all over the area, as depicted in II, which can reveal the increasing of electrical output until reach the highest values. Meanwhile, the increasing of filler's amount above the  $p_c$ , showing the irregular dispersion which some agglomeration. It exhibits an unable improvement in the output efficiency, as shown in III.

Overall explanation can be given to the connection of conductive polymer. After the fabric was composited with conductive polymer, the charges carrier was generated. The generated charges cannot flow easily with non-connection path by irregular connection of filler particles. A suitable amount of conductive polymer filler can be a suitable pathway leading the flowing of the charges from one to other fillers until reaching the load. The addition of fillers higher than the  $p_c$  leads to the overflow amount of charge carriers. Some charge carriers could directly export to external load, while the others are opposed together, leading the scattering charges to inappropriate to export to the external load. Another point of interest is that the same type of conductive polymers of PANI show different percolation points owing to the different types of cellulose-based fabric matrix phase. Therefore, the Rayon/PANI have a critical condition at PANI 0.25 g, while the cotton/PANI represent at PANI 0.15 g condition of the percolation threshold. These results are corresponding with other research that the CB composite with different types of polymers relative to the contrast amount of percolation threshold (130).

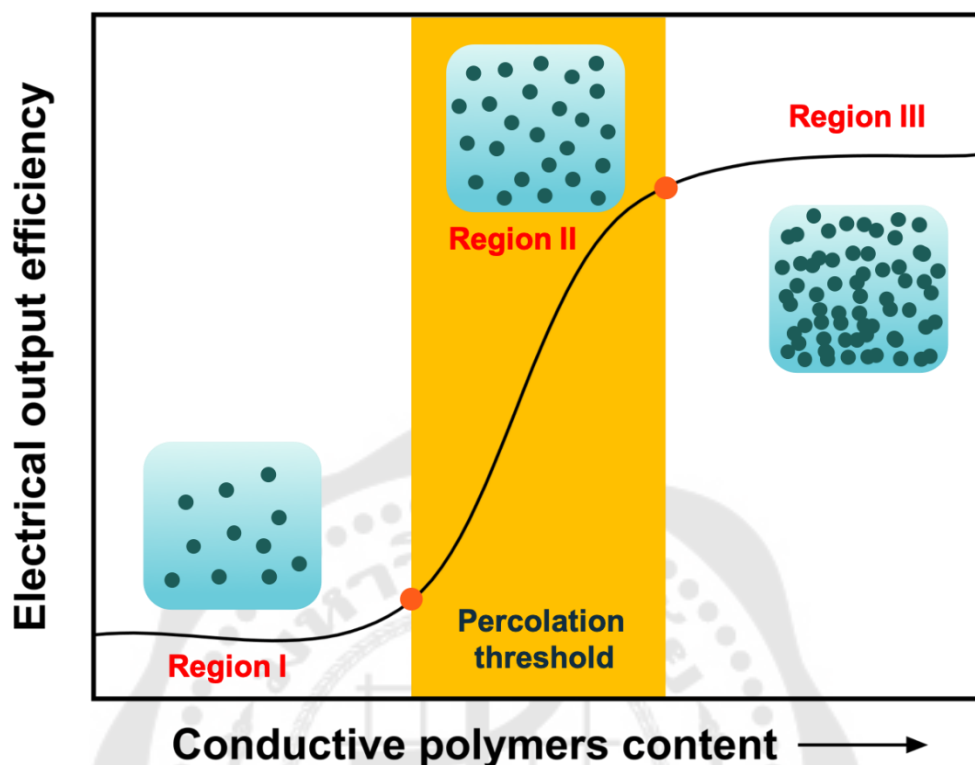


Figure 130 Percolation threshold explanation of conductive polymers content filler relative to electrical output efficiency

Furthermore, to combine the scientific discussion of thermoelectric mechanism with working mechanism of LS-mode TENG as present as the hybrid TENG-TEG, the vector graphic was illustrated in Figure 131. As in initial state (state I), the full contact of cellulose-based/conductive polymers fabric with Teflon film generate the positive and negative charges on each surface, respectively. The creation of both charges is equal to no exporting of charges. While the sliding motion is set up, the two layers sliding outward and electrostatic induction was created with induced the opposite charges to both electrodes. Moreover, while the two layers are sliding along each other (state II), the heat is then generated (Red zone) with thermoelectric effect of P3HT and PANI. The delocalized electron of P3HT and PANI hop along the molecular structure and generate the holes which is positively charge (86,132). During a full motion of sliding (state III), the holes were generated more and contained in the band. Then the charges move to the

cooler side of conductive fabric electrode and produce an electrostatic induction. The generation of a potential difference was driven the electron to export throughout the external load, producing the signal of positive current. Subsequently, the ongoing of opposite slide motion in state IV, the charges are continuously flowing. Whereas the charges from Al tape move backward to the conductive fabric electrode, building the signal current of negative within AC waveform. The mechanism exhibits that the addition of p-type conductive polymers creates the holes that expands the charge concentration on cellulose-based fabric/conductive polymers. It can conclude that, the fabrication of hybrid TENG-TEG device by composite conductive polymers including P3HT, PANI and PANI/CNT with cellulose-based fabric capability to improve higher electrical output performance comparison to traditional TENG device.

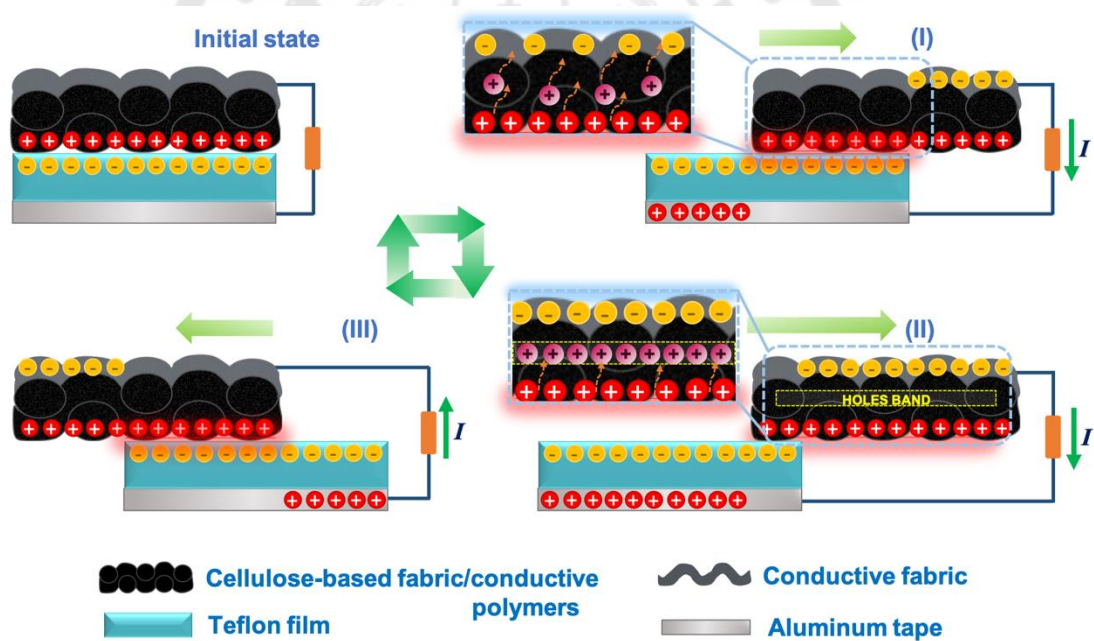


Figure 131 The working mechanism of LS-mode TENG incorporates thermoelectric effect of hybrid TENG-TEG system

## CHAPTER 5

### CONCLUSIONS

In this work, the cellulose-based fabrics of Rayon and cotton fabrics were selected owing to the consisting of hydroxyl groups as main functional group. The conductive polymers which act as thermoelectric materials, including P3HT, PANI and PANI/CNT were used to incorporate into the fabrics for electrical output performance's enhancing. The composite fabrics in various systems of Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT were studied. All conductive polymers and composite fabrics were characterized to investigate the morphology and chemical structure characteristics. The physical property and surface morphology of fabrics was observed by color spectrometer, LOM and SEM. The functional group and chemical bonding were examined by ATR-IR, Raman spectroscopy and XRD. Because various amounts of conductive polymers were studied, the thermoelectric properties, electrical properties and electrical output efficiency were also investigated relatively. After reporting and discussing in the last chapter, all the results can be summarized by following the list of 5.1-5.6.

#### **5.1 The result of preparing conductive polymers and conductive polymers/CNT composite**

In this work, two types of conductive polymers consisting of P3HT and PANI were selected. Firstly, the commercial P3HT rough powder, it was grinded into fine powder by mortar and pestle. Next, the preparation of PANI and PANI/CNT was successfully synthesized by using chemical polymerization method. The aniline solution is doped with acid dopant of HCl and obtained the p-type PANI powder. While the addition of CNT to aniline solution, receiving the p-type PANI/CNT powder.

#### **5.2 The result of characteristic of conductive polymers and conductive polymers/CNT**

According to the characteristic of conductive polymers and conductive polymers/CNT, the characterization was separated into morphological and chemical structure characterization.

### 5.2.1 Morphological of conductive polymers and conductive polymers/CNT

The results of morphology of conductive polymers and conductive polymers/CNT including P3HT, PANI and PANI/CNT were observed by SEM technique. The P3HT powder shows coarse powder within unique color of dark purple. The PANI powder shows branch-shape of secondary particles from compacted primary particle that are arranged together in network. The PANI of fine dark green powder shows branch-shape of secondary particles from compacted primary particle that are arranged together in network. Whereas the PANI/CNT demonstrates a semi-circular shape of PANI particle with a numerous tube of the CNT wrapping around particles, presenting the CNT composite.

### 5.2.2 Chemical structure characterization of conductive polymers and conductive polymers/CNT

In addition, the results of chemical structure were examined by ATR-IR, Raman and XRD. According to the study of P3HT present the ATR-IR evident peak at  $1390\text{ cm}^{-1}$ , which correlates to the characteristic of thiophene ring in P3HT molecular structure. Also, the quinoid ring is assigned to the stretching mode vibration of C-S-C and C=O group where at  $960\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$ , which are symbolize the P3HT molecular structure. Although, the ATR-IR results of PANI and PANI/CNT are identified in a region of  $4000\text{-}500\text{ cm}^{-1}$ . The attribution of C=O stretching, C=N stretching and C-N stretching which corresponds to the aromatic amine in PANI and PANI/CNT was found. The Raman spectra supported the CNT characteristic of D-band and G-band. While the XRD pattern present the crystalline part of semi-crystalline PANI structure, belonging to (121), (113) and (322) crystal plane.

### 5.3 The result of preparing cellulose-based fabric and cellulose-based fabric/conductive polymers

In this work, the cellulose-based fabrics were prepared by desizing and scouring process. Consequently, the conductive polymers including P3HT solution, PANI solution and PANI/CNT solution was also prepared. The ultrasonicate dip-coating process is used to composite the cellulose-based fabric with conductive polymers and

conductive polymers/CNT. All of the composite system consisting of Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT was successfully prepared. On the other hand, the Rayon/P3HT/CNT and Rayon/PANI/CNT system failed to construct owing to the high-cost of commercial P3HT powder and the irregular distribution between Rayon fabric and conductive polymers/CNT. Also, the Rayon/PANI demonstrate the fluctuation results between electrical properties and electrical output efficiency. The reason for these results is given to the coating ability and dispersibility of PANI particle over the Rayon fabric surface that the PANI are irregularly dispersed. So, the cotton/PANI/CNT are selected as three phases composite system for comparison and solve the problem of fluctuation results.

#### **5.4 The result of characteristic of cellulose-based fabric and cellulose based fabric/conductive polymers**

The cellulose-based fabric/conductive polymers was separated into two main system, consisting of cellulose-based fabric/P3HT (Rayon/P3HT) and cellulose-based fabric/PANI (Rayon/PANI, Rayon/PANI/CNT, cotton/PANI and cotton/PANI/CNT). The characteristic's discussion focused on the physical properties, surface morphology and chemical structure characterization.

##### **5.4.1 The Morphological of cellulose-based fabric and cellulose based fabric/conductive polymers**

In this work, the physical properties result of cellulose-based fabric and cellulose-based fabric was measured by color spectrophotometer. The result shows the different shade of color, presenting in contrast lightness values. The surface morphology of cellulose-based fabric was studied by LOM and SEM, consisting of Rayon and cotton fabric. The LOM and SEM result demonstrate an orderly arrangement of cellulose fibers. It shows an average fiber size about  $13.4 \pm 0.57 \mu\text{m}$  and  $12.65 \pm 3.62 \mu\text{m}$  of Rayon and cotton fiber, respectively. Whereas the SEM results of cellulose-based fabric/conductive polymers demonstrate the small particles packing over the surface of fabric and also

between each fiber. Meanwhile, the larger packing number of conductive polymers relates to an increasing of conductive polymers content.

#### **5.4.2 The chemical structure characterization of cellulose-based fabric and cellulose based fabric/conductive polymers**

Furthermore, the results of chemical structure were examined by ATR-IR, Raman and XRD. The study reported that the ATR-IR functional peak of conductive polymers is not obviously indicate the characteristic. On the other hand, the Raman at a region of  $500\text{-}2000\text{ cm}^{-1}$  show the fingerprint of P3HT, PANI and PANI/CNT which attributed by C-S-C group, and C=N group with G-band and D-band, respectively. For more clearly results, the XRD pattern also support the studying of Raman technique that demonstrate the crystalline peak of semi-crystalline PANI with the characteristic peak of cellulose-based fabrics.

#### **5.5 The result of flexible hybrid TENG-TEG device fabrication**

The hybrid TENG-TEG was successfully fabricated by comprising two TENG layers. The upper layer consists of cellulose-based fabric/conductive polymers including Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT, serving as tribo-positive contact layer. Meanwhile, the bottom layer of a tribo-negative contact layer is using Teflon film. Both upper and bottom contact layers are affixed with conductive fabric and Al tape to act as each electrode. The operation mode of this hybrid TENG-TEG device is present under the working structure of lateral sliding mode (LS-mode) with flexibility. The two contact layers are aligned parallel to each other and are moved along both edges through mechanical motion. In this LS-mode mechanism, the bottom part remains fixed while the top part undergoes sliding motion.

#### **5.6 The results of the effect of adding conductive polymers and conductive polymers/CNT to the fabrics on the performance of hybrid TENG-TEG devices**

In this work, the cellulose-based fabric/conductive polymers hybrid TENG-TEG system are represented in various system. The results show that while adding

conductive polymers and conductive polymers/CNT to cellulose based fabric, both electrical properties and output efficiency increased in values.

#### **5.6.1 The effect of adding conductive polymers and conductive polymers/CNT to the fabrics on the electrical properties**

The electrical properties including the impedance and conductivity of various successfully system consisting of Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT were concluded in this section.

##### **5.6.1.1 The electrical properties of Rayon/P3HT**

The impedance of Rayon/P3HT system are not represented in form of semi-circular loop but performed in nearly vertical line with different diameter. The pristine Rayon fabric possesses the highest resistivity with a longest diameter at higher frequency. By adding P3HT to Rayon fabric, the Rayon/P3HT-150 mg show the smallest diameter of impedance loop, presenting lowest in resistivity. The results confirm that the resistance of Rayon/P3HT composite fabrics decreased with an extending of P3HT content. Moreover, the impedance of Rayon/P3HT-150 mg was measured at difference temperature. It can conclude that the presence of lowest impedance value occurred at 40°C. Hence, the use of Rayon/P3HT in the application of TENG-TEG device to create the 40°C of temperature by sliding contacting is possible.

The conductivity as a function of frequencies at room temperature is presented in this system. At low frequency of 100 Hz, the pristine Rayon fabric provide the lowest conductivity. Meanwhile, the frequency increased with a rising of conductivity. So, at highest frequency, the conductivity of pristine Rayon fabric was increased to  $1.7 \times 10^{-4}$  mS/cm. All of the Rayon/P3HT also behave in a same trend with an increasing of conductivity comparing to pristine Rayon fabric. Moreover, as the P3HT content rises, the conductivity is also increased. Whereas the highest conductivity of  $3.5 \times 10^{-4}$  mS/cm was given by Rayon/P3HT-150 mg, which is 2 times greater than that of pristine Rayon fabric. Therefore, it can conclude that an additional P3HT filler can significantly improve both impedance and the conductivity of the pristine Rayon.

### 5.6.1.2 The electrical properties of Rayon/PANI

In each impedance loop of Rayon/PANI, the different resistivity was represented with difference in diameter. Pristine Rayon fabric exhibits the highest resistivity with the largest loop's diameter. Conversely, the smallest in diameter's loop was given to the Rayon/PANI 0.50 g. The results reported the reducing of the loop's diameter does not depend on an increasing of PANI content but depend on the optimum amount of PANI content.

To confirm the trend of impedance, the electrical conductivity of Rayon/PANI fabrics are relative with a range of frequencies. At high frequency, the conductivity of both pristine Rayon fabric and Rayon/PANI fabric for all conditions rise in the exponential trend. This result exhibits that the pristine Rayon fabric provides the lowest conductivity values of  $4 \times 10^{-6}$  S/cm, while the highest was generated by Rayon/PANI 0.75 g at  $> 5 \times 10^{-6}$  S/cm. However, the other conditions of composite fabrics not behaved to the relation of increasing content of PANI. However, the trend of conductivity results does not correlate with the impedance trend. So, the study of electrical output performance is introduced for clearer reasons.

### 5.6.1.3 The electrical properties of cotton/PANI

The impedance results reported in form of the semi-circular loops of cotton/PANI for all conditions. Firstly, the pristine cotton fabric exhibits the highest resistivity with the largest loop's diameter. Meanwhile, adding more amount of PANI content to the cotton fabric presented a decreasing in diameter's loop. Conversely, the smallest in diameter's loop was given to the Rayon/PANI 0.75 g. The results show that the reducing of the loop's diameter depend on an increasing of PANI content. So, the Rayon/PANI 0.75 g reach the lowest resistivity while pristine cotton reveals the highest in resistivity value in this system.

The impedance could confirm the trend along with the electrical conductivity, the conductivity of both pristine cotton fabric and cotton/PANI fabric rise in the exponential trend. The lowest conductivity of  $4.3 \times 10^{-7}$  S/cm was given by pristine

cotton, while the highest was generated by cotton/PANI 0.75 g at  $2.8 \times 10^{-5}$  S/cm. All of conductivity results show the behaved exponential graph with relation to an increasing of PANI contents. Moreover, the electrical conductivity results show the same tendency of with impedance results. It can be concluded that the additional of PANI to cotton fabrics can improve the electrical properties including the impedance and electrical conductivity.

#### 5.6.1.4 The electrical properties of cotton/PANI/CNT

At low frequency, the pristine cotton fabric demonstrates the largest loop, where the cotton/PANI/CNT 1.50 g shows the smallest. The evident loop can conclude that resistivity is decreased with an increase of PANI/CNT content. The cotton/PANI/CNT 1.5 g show the lowest resistivity in this case. In addition, the Z of cotton/PANI/CNT 1.5 g with the function of temperature. At room temperature, the Z of cotton/PANI/CNT 1.5 g reveals the highest value. While Z get decrease in lowest values at  $60^{\circ}\text{C}$ . It can conclude that the Z' values is not correlate to the rising temperature but depends on the normal working temperature of each thermoelectric materials.

The results demonstrate that the conductivity significantly increases with the increasing of PANI/CNT content on cotton fabric. The pristine cotton indicated poor conductivity at a frequency of 1MHz. The cotton/PANI/CNT 1.50 g provided the highest conductivity of  $\sim 1.04$  mS/cm. Furthermore, the conductivity at different temperature of cotton/PANI/CNT 1.50 g was analyzed. The lowest conductivity was generated at RT, while reaching a peak at  $60^{\circ}\text{C}$ . This is evident that the conductivity values exhibited with the consistent trend of the impedance, relative to the varying of temperature. Notably, the electrical properties of the impedance and conductivity depend on the containing of PANI/CNT content, leading the cotton/PANI/CNT 1.50 g has the best performance compared with other conditions.

### 5.6.2 The effect of adding conductive polymers and conductive polymers/CNT to the fabrics on the electrical output efficiency

The electrical output including the  $V_{OC}$ ,  $I_{SC}$  and  $P_{max}$  of various system consisting of Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT were concluded in this section.

#### 5.6.2.1 The electrical output efficiency of Rayon/P3HT

The electrical output efficiency of Rayon/P3HT are measured into two system of unheated and heated system. The highest electrical output was enhanced in difference conditions. Among the Rayon/P3HT hybrid device (Unheated system), the best output is provided at 49.50 V and 35  $\mu$ A while at heated system, the highest output reveals at 62.96 V and 45  $\mu$ A by Rayon/P3HT-150 mg composite fabric which is 1.5 times higher than pristine Rayon fabric. Meanwhile, the  $P_{max}$  of pristine Rayon fabric is revealed approximately  $\sim 114.5 \mu$ W at  $1M\Omega$ , whereas the Rayon/P3HT-150 mg shows a maximum value about  $\sim 1204.1 \mu$ W at the same resistance of  $1M\Omega$ . The Rayon/P3HT-150 mg could generate the  $P_{max}$  by 10.5 times larger than that of the pristine Rayon fabric.

#### 5.6.2.2 The electrical output efficiency of Rayon/PANI

According to the Rayon/PANI system, the pristine Rayon fabric reveal the lowest output efficiency. The  $V_{OC}$  and  $I_{SC}$  of Rayon fabric reveals at 34.9 V and 16  $\mu$ A, respectively. Whereas the Rayon/PANI 0.25 g which is an optimum condition reaches the highest values of both  $V_{OC}$  and  $I_{SC}$  about 45.1 V and 72.8  $\mu$ A. Moreover, for the output power, booth pristine Rayon and Rayon/P3HT 0.25 g have a specific load resistance at  $1M\Omega$ . The pristine Rayon fabric indicates  $P_{max}$  of 114.50  $\mu$ W while the Rayon/PANI 0.25 g achieve the  $P_{max}$  of 171.12  $\mu$ W which is 1.5 times higher value than that of pristine Rayon fabric. It can conclude that, while increased the PANI content of 0.25 g, the output efficiency of pristine Rayon fabric can improve.

### 5.6.2.3 The electrical output efficiency of cotton/PANI

As the output efficiency of cotton/PANI was measured, the result show that, the pristine cotton fabric provides about 11.18 V and 16  $\mu$ A. The 3 times higher in output efficiency of pristine cotton was performed by the cotton/PANI. Hence, the  $V_{OC}$  and  $I_{SC}$  of cotton/PANI 0.15 g show at 34 V and 47  $\mu$ A which is the optimum condition in this system.

### 5.6.2.4 The electrical output efficiency of cotton/PANI/CNT

According to the output efficiency measurement of cotton/PANI/CNT, the two system of unheated and heated system was mentioned. In unheated system, the highest output was generated at 32.96 V and 39.96 mA by cotton/PANI/CNT 1.5 g. Also, in heated system, the cotton/PANI/CNT 1.5 g shows the beat output provided at 50.09 V and 77.34 mA which is 3.7 and 2.5 times higher than the  $V_{OC}$  and  $I_{SC}$  of pristine cotton fabric. In addition, the  $P_{max}$  of pristine cotton fabric reveal approximately 49.6  $\mu$ W based on the external load resistance of  $1M\Omega$ , whereas the  $P_{max}$  of 263  $\mu$ W was generated by cotton/PANI/CNT 1.5 g. It demonstrates a higher value than that of pristine cotton by 5.3 times, due to composite of PANI/CNT

The output efficiency of cellulose-based fabric/conductive polymers and cellulose-based fabric/conductive polymers/CNT possess higher values than pristine cellulose-based fabric owing to the additional of conductive polymers and conductive polymers/CNT. The conductive polymers effect the electrical output by generating more charge carriers combine with triboelectric charges. Leading the cellulose-based fabric/conductive polymers behave better electron donor ability to contact with electron acceptor materials. Also, the incorporation between triboelectrification and thermoelectric effect could promote the electrical output, confirming the improvement of hybrid TENG-TEG for all system in this work.

## 5.7 Suggestion and future perspective

In this thesis study the enhancement of TENG by using the composite fabrics between cellulose-based fabric and different types of conductive polymers to act as hybrid TENG-TEG system within lateral-sliding mode. Various of composite system (Rayon/P3HT, Rayon/PANI, cotton/PANI and cotton/PANI/CNT) in this work was studied and successfully prepared. The results indicated that these composite fabrics hybrid TENG-TEG device have an efficiency to promote the output performance than traditional TENG device. But the limitations are also taking place with some composite system consisting Rayon/P3HT/CNT and Rayon/PANI/CNT which are unsuccessful construct. The reason is given to the costly of commercial P3HT and also an irregularly dispersion of conductive polymers/CNT to Rayon fabrics. For the suggestion, each conductive polymer should be selected with a suitable type of cellulose-based fabric to perform effectively coating ability which effect to the interesting electrical properties and output performance. However, there still having a gap to optimize the efficiency and develop the device as a practical application used with human body. First of all, fitting in the working mechanism of hybrid TENG-TEG device with the body's functions is an important key. In addition, the component of hybrid device should be fully flexible with all compatible materials and washability. Along with these aspects, the electrical output of hybrid TENG-TEG system in this thesis work reveals high performance, leading to have a chance to advance into E-textiles system for commercial in the future.

## APPENDIX





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