

INTEGRATED MULTILAYER TRIBOELECTRIC NANOGENERATOR FROM BIO-BASED COMPOSITES FOR MECHANICAL ENERGY HARVESTING TECHNOLOGY

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2024



อุปกรณ์ผลิตพลังงานไฟฟ้าขนาดเล็กชนิดไทรโบอิเล็กทริกโครงสร้างหลายชั้นในตัว ในกลุ่มวัสดุ ชีวภาพคอมโพสิต สำหรับเทคโนโลยีการเก็บเกี่ยวพลังงานเชิงกล



ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร วิทยาศาสตรมหาบัณฑิต สาขาวิชาวัสดุศาสตร์ คณะวิทยาศาสตร์ มหาวิทยาลัยศรีนครินทรวิโรฒ ปีการศึกษา 2567 ลิขสิทธิ์ของมหาวิทยาลัยศรีนครินทรวิโรฒ INTEGRATED MULTILAYER TRIBOELECTRIC NANOGENERATOR FROM BIO-BASED COMPOSITES FOR MECHANICAL ENERGY HARVESTING TECHNOLOGY



A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of MASTER OF SCIENCE (Materials Science) Faculty of Science, Srinakharinwirot University

2024

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THE THESIS TITLED

INTEGRATED MULTILAYER TRIBOELECTRIC NANOGENERATOR FROM BIO-BASED COMPOSITES FOR MECHANICAL ENERGY HARVESTING TECHNOLOGY

ΒY

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HAS BEEN APPROVED BY THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE MASTER OF SCIENCE IN MATERIALS SCIENCE AT SRINAKHARINWIROT UNIVERSITY

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Title	INTEGRATED MULTILAYER TRIBOELECTRIC NANOGENERATOR FROM BIO-
	BASED COMPOSITES FOR MECHANICAL ENERGY HARVESTING
	TECHNOLOGY
Author	NATDANAI SUKTEP
Degree	MASTER OF SCIENCE
Academic Year	2024
Thesis Advisor	Assistant Professor Dr. Thitirat Charoonsuk

In the past three years, medical electronic devices has been extensively developed for realtime diagnosis and health monitoring. Since their physical design requires flexibility, stretchability, and lightweight properties, finding an alternatively electrical power source to replace the use of battery has become one of the key issues to be addressed. Triboelectric nanogenerator (TENG), which can harvest the mechanical energy from rubbing to produce electricity, is focused in this work. Biomaterials such as silk fibroin (SF) and bacterial cellulose (BC) were selected as the main friction layers. However, most biomaterials still provide low electrical output. Therefore, the aim of this study was to enhance the electrical output of these biomaterial TENG through two strategies: (1) incorporating the dielectric magnesium aluminum layer double hydroxide nanosheet (MgAI LDH NS) to improve electrical output by improving dielectric constant, and (2) modifying the device structure to be multilayer TENG (M-TENG) by inserting charge-trapping layer between friction layer and electrodes. For the first strategy, higher dielectric constant of MgAI LDH successfully enhanced the maximum output power (Pmax) of SF/MgAI LDH and BC/MgAI LDH, by increasing charge density. The SF/MgAI LDH at 3% achieved the P_{max} of about 165 μ W (power density = 18.3 μW/cm²), while the BC/MgAI LDH at 1.5% generated 542 μW (power density of 60.2 μW/cm²). Once the optimal conditions were established, the second strategy was focused on the M-TENG design. SF/lignin composite film was inserted between SF/MgAI LDH film and its electrode. Similarly, the BC/lignin was used for the BC-based system. The results clearly showed that inserting charge-trapping layer of SF/lignin and BC/lignin further improve electrical output. The SF-based M-TENG produced a P_{max} of 205 μ W (22.8 µW/cm²), which is 1.2 times higher than that of SF/MgAI LDH. Likewise, inserting BC/lignin between BC/MgAI LDH and electrode generated a P_{max} of 918 μ W (102 μ W/cm²). It is almost 26 times higher than BC/MgAI LDH 1.5%(v/v). The aromatic ring from lignin structure helped retain the charge, preventing its loss before orderly transfer to the load. Finally, the results of this work confirm the potential of using biomaterials for high efficiency power supply for small electronic devices as demonstrated by the ability to power more than a hundred LED.

Keyword : Silk fibroin, Bacterial cellulose, Layer double hydroxide, MgAI LDH, Multilayer TENG

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to my thesis advisor, Asst. Prof. Dr.Thitirat Charoonsuk and Prof. Dr.Naratip Vittayakorn, for their unwavering support, guidance, and invaluable insights throughout the course of my research. Their expertise, patience, and encouragement were fundamental to the completion of this work. I am also sincere thanks to Assoc. Prof. Dr.Tosapol Maluangnont for his advice in the part of nanodielectric nanosheet information. Also, I am grateful to Dr. Phakkhananan Pakawanit for helping with SR-XTM technique and her encouragement.

I would also like to thank the members of my thesis committee, Prof. Dr.Naratip Vittayakorn (Chairman) and Assoc. Prof. Dr.Natthapong Phinichka (Committee), for their constructive feedback and suggestions, which helped to refine my research and significantly improved the quality of this thesis.

Also, I am especially grateful to all the lecturers in the Department of Materials Science, Srinakharinwirot university for providing the resources and academic environment necessary for the success of this project. This research would not have been possible without the financial support the Office of the Permanent Secretary, Ministry of Higher Education, Science, Research, and Innovation (OPS MHESI), Thailand Science Research and Innovation (TSRI), and Srinakharinwirot University under the Grant number RGNS 64-211. I would also like to thank the facilities and technical assistance from the Nanotechnology and Materials Analytical Instrument Service Unit (NMIS) of College of Materials Innovation and Technology, KMITL. I truly appreciate their belief in my work and the opportunity to conduct this research.

Additionally, I am deeply thankful to every member of Advanced Materials Research (AMR) group, especially to Prof. Dr.Naratip Vittayakorn for accepting me to the research group and encouragement. I am also grateful to my colleagues and friends, particularly Miss Jitrawan Noisak, Miss Suchanat Navatragulpisit, Miss Sirinya Ukasi, Miss Apichayaporn Teandam, and Miss Rawiwan Khwanming, for their intellectual support, encouragement, and camaraderie during the more challenging times. Your friendship and insight were invaluable.

While this thesis is the result of the support and guidance of many people, I would also like to acknowledge my own efforts in the completion of this work. The journey of writing this thesis required perseverance, discipline, and resilience, and I am proud of the growth I experienced throughout this process. There were moments of doubt and challenge, but through dedication and a passion for the research, I was able to push through and reach this significant milestone. This experience has not only expanded my knowledge but also shaped my personal and academic development. I am grateful for the opportunities this research has provided me and for the strength I found within myself to overcome obstacles and complete this thesis.

Lastly, I want to express my deepest appreciation to my family, thank you for your endless love, encouragement, and belief in my abilities. Your support was my constant source of strength throughout this journey. To my friends and loved ones, thank you for your patience and understanding during the intense phases of this work.

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CHAPTER 1 INTRODUCTION

Background and significance of the research

In the present time, the rapid development of healthcare Internet of Things (H-IoT) technology becomes a pressing demand for human health (1) and health care monitoring (2, 3). During the forecast period (2023 to 2030), the global of H-IoT market is expected to grow at a significant CAGR of 20.4% (4). However, the power supply technology is a critical challenge in the implementation of H-IoT applications because of its demand for a steady power to enable long-term connectivity with safe and noninflammation devices (5). Energy harvesting technology referred to the conversion of the unused ambient energy into useful electrical energy (6) is proposed with benefits and challenges (7). In 2012, Prof. Dr. Wang and his research team discovered the triboelectric nanogenerator (TENG) (8), the one of mechanical energy harvesting (MEH) devices, to collect the mechanical energy and transform into electricity. The mechanical energy can be converted into electrical energy via the triboelectric effect by using two different materials with different electron donor and acceptor abilities to provide charge transfer. Biomaterials have been considered as promising materials for the construction of the next generation of flexible TENG to open up opportunity for utilizing in field of medical electronics and healthcare device. Rice paper (9), bacterial cellulose (BC) (10), chitosan (11), and silk fibroin (SF) (12) have been raised focus on the past decade. Among those biomaterials, the SF and BC are attention in this work owing to their occupying the strong electron-donating tendency from the amine group (-NH2) and hydroxyl group (O-H) (13).

In the past decade, several studies have been carried out on TENG based on SF and BC for proposing as tribo-positive side on charge generating layer. Several methodologies for fabrication SF are developed including solution casting (14-16), spin coating (17), and spray coating (18). Meanwhile, the fabrication process of BC is mainly proposed based on biosynthesis from bacterial strain of *Komagataeibacter nataicola* (TISTR 975) (19), and *Acetobacter xylinum* (KJ1) (20-22). The electrical output including the open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}), was provided in range about 25 to 172 V and 0.3 to 8.5 µA for SF-based TENG, and 15 to 55 V with 0.2 to 4 µA for BC-based TENG. As can be seen from the literature, the biomaterials SF and BC show potential to be charge generating in TENG. Nevertheless, the present performance and lifetime of SF- and BC-based TENG is significantly lower than that of conventional TENG prepared from synthetic polymer (23). Achieving higher quality and better performance of SF- and BC-based TENG needs to be concerned without destroying environmental and biocompatibility (24). To accomplish this, searching for increasing the efficiency of the charge generating layer through chemical and physical methods by material selection (25), surface modification (26), chemical functionalization (27), composite material fabrication and structural design (28) is now interesting.

However, surface modification and chemical functionalization techniques are suffered from several unfavorable limitations, such as expensive with sophisticated instruments, time-consuming, complicated procedures, in addition with highly trained technicians to perform (29). So far, compositing is the most common method that is used for enhancement of charge generating layer by adding fillers. The dielectric material, which are capable of creating the polarization within the material when exposed to an external electric field (30), is famous. The previous work has succeeded the enhancement of composite TENG by incorporating dielectric materials and piezoelectric materials such as ZnO (21), BaTiO₃ (BT) (31), TiO₂ (32), Al₂O₃ (33). Among a diverse library of nanomaterial fillers, two-dimensional nanosheets (2D NS) are an encouraging prospect in case of achieving the thin and flexible film fabrication. The titanium oxide NS is proposed with an attractive result due to the outstanding of dielectric property with large relative dielectric constant about 125 as reported by Osada et al. (34). In the subsequent work, S. Sriphan et al. demonstrated the flexible TENG with using filter paper (35), BC (32) and polydimethylsiloxane (PDMS) (36) as friction layer. By incorporating the Ti_{0.8}O₂ NS, the electrical output performance was

higher than the unincorporating filler in TENG device. Also, a layer double hydroxide nanosheets (LDH NS), another type of 2D NS (37, 38), has been proposed owing its interested dielectric properties, larger adsorption capacity, non-toxicity, cost-effectivity and simplicity in fabrication (39). LDH is usually represented by the formula $[M^{2+}_{,(1-x)}M^{3+}_{,x}(OH)_2]^{x+}(A^{n-}_{,x/n})\cdot mH_2O$, where Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , etc., and Al^{3+} , Cr^{3+} , Fe^{3+} , V^{3+} , Co^{3+} , etc. are normally indicated in basic layers of these compounds. Since, the ionic radii of Mg^{2+} can form stable with Al^{3+} , the design and preparation of MgAI LDH NS were usually carried out. Because of its good insulating properties (bandgap 4.6 eV) and dielectric constant about 40 (40, 41), MgAI LDH is now interested. In 2020, Cui and their team (42) were fabricated the modified-TENG by direct growing the MgAI LDH NS on a aluminum substrate. The modified-TENG could generate higher the V_{oc} , and the current density of 13 V, and 1.6 μ A/cm² as compared to the unmodified TENG.

Nevertheless, the enhancement of charge generating layer arises rather limitation, due to the charge on the contact layer disappears during contact and separation process. The temporary charges can be lost and recombined between charge generating layer and electrode (43). The structural design in form multilayer TENG (M-TENG) is a potential way to improve the electrical output efficiency. In the subsequent work, Cui et al. designed the multilayer composite structure for TENG (M-TENG) device by inserting charge trapping layer between charge generating layer, including polyvinylidene fluoride (PVDF) (44), poly(vinyl) alcohol (PVA) (45), polystyrene (PS) (46), and electrode. It was found that PS can be the effective charge trapping layer owing to its charge storage ability. The current density was provided in the range of 0.05 to 0.07 μ A/cm² higher than TENG without charge trapping layer for 2.6 to 7 times. respectively. The scientific discussion is provided by containing the aromatic ring in polymers. A large number of trapping sites from aromatic rings can trapped more charged and hole for a while before transferring to the load. This mechanism can prevent the recombination process (46). Therefore, adding trapping layer is interested in the structural design for TENG.

In this work, the biomaterials-based composite based on SF and BC systems is fabricated as charge generating layer for flexible TENG (F-TENG). The combination of two strategies; 1) modification of charge generating layer and (2) multilayer structural design is proposed with inserting charge trapping layer. SF and BC films are modified by incorporating various amounts of MgAI LDH NS of 0.5 to 12% (v/v) to find the optimum condition for achieving the highest electrical output. The characteristics of the materials are identified. The functional groups and the fingerprint of MgAI LDH NS and its composites is confirmed by the attenuated total reflection-infrared spectroscopy (ATR-IR) and Raman Spectroscopy (Raman). The phase identification and crystal structure are analyzed by X-ray diffraction (XRD). The transmittance of the samples is measured by UV-Vis spectroscopy instrument. The energy gap is determined indirectly by using Tuac's equation. The surface and cross-sectional morphology of the samples is studied by the scanning electron microscope (SEM) . The distribution of MgAI LDH NS in biomaterial composite films is analyzed by Synchrotron radiation X-ray tomographic microscope (SR-XTM). The 3D virtualization is imaged by running Distri software. The effect amounts of MgAI LDH NS and charge trapping layer on the electrical output signal, including the open-circuit output voltage (V_{oc}), short-circuit output current (I_{so}) and maximum output power (P_{max}) of all the samples are investigated by using oscilloscope and digital multimeter (DMM) in the vertical contact separation mode (VCS). Additionally, the bio-based composite M-TENG has the capacity to power up to 120 LEDs connected in series and can be used as a power source to power a variety of small electronic devices. The M-TENG device's excellent performance in this work gives us hope for the future as we move toward developing bio-based systems for commercial application.

The objective of the study

1. To study the synthesis of MgAI layer double hydroxide nanosheets (LDH NS).

2. To prepare the Bio-Based composite films by incorporating MgAI LDH NS.

3. To characterize of the MgAI LDH NS incorporated Bio-Based composite films.

4. To fabricate the flexible triboelectric nanogenerator (F-TENG).

5. To study the effect of MgAI LDH NS addition on the electrical output signal of the Bio-Based composite F-TENG.

6. To fabricate multilayer structure of F-TENG by inserting charge trapping layer.

7. To study the effect of charge trapping layer on the electrical output signal of the multilayer F-TENG.

Scope of the study

1. Synthesize the MgAI LDH NS via co-precipitation method.

2. Prepare the Bio-Based composite film based from silk fibroin (SF) and bacterial cellulose (BC) by adding various amount of MgAI LDH NS from 0.5 to 12% (v/v).

3. Study the characteristic of the SF and BC composite films by attenuated total reflection-infrared spectroscopy (ATR-IR), Raman Spectroscopy (Raman), X-ray diffraction (XRD), UV-Vis spectroscopy instrument, scanning electron microscope (SEM) and synchrotron radiation x-ray tomographic microscope (SR-XTM).

4. Fabricate the flexible triboelectric nanogenerator (F-TENG) based on the vertical contact separation mode (VCS).

5. Study the effect of the addition of MgAl LDHs NS in SF and BC composite on the electrical output performance, including the open-circuit output voltage (V_{oc}), short-circuit output current (I_{sc}) and maximum output power (P_{max}) of the biomaterial composite F-TENG.

6. Fabricate multilayer structure of F-TENG by inserting Bio-based composite films by adding lignin powder as a charge trapping layer.

7. Study the effect of charge tapping layer amount on the electrical output performance by measuring V_{oc} , I_{sc} and P_{max} of the multilayer F-TENG.



Conceptual Frameworks

Figure 1 Conceptual framework

Expected Outcome

1. Obtain the MgAI LDH NS via co-precipitation method.

2. Obtain the Bio-Based composite film with incorporating various amount of the MgAI LDH NS from 0.5 to 12% (v/v).

3. Obtain the characteristics of the Bio-Based composite films.

4. Achieve the flexible triboelectric nanogenerator (F-TENG) based on the vertical contact separation mode.

5. Understand the effect of the various amount of MgAI LDH NS on the electrical output performance and the optimum amount of the F-TENG.

6. Achieve the multilayer structure of F-TENG by inserting Bio-based composite films by adding lignin powder as a charge trapping layer.

7. Understand the effect of charge tapping layer amount on the electrical output performance and the optimum amount of the F-TENG.



CHAPTER 2 LITERATURE REVIEW

2.1. Healthcare Internet of Things (H-IoT)

Healthcare Internet of Things (H-IoT) is a rapidly expanding field that combines internet-enabled devices, sensors, and software applications in the healthcare industry. It aims to enhance patient outcomes, increase efficiency, and reduce expenses by providing real-time data, predictive analytics, and remote monitoring. H-IoT include wearable devices, remote patient monitoring, telemedicine, and intelligent hospital systems. From the systems involve data collection, storage, analysis, and dissemination to detect early signs of disease, monitor patients remotely, and personalize treatment plans, as shown in Figure 2. (47). The global H-IoT market is expected to reach approximately \$960.2 billion by 2030, with a compound annual growth rate (CAGR) of 20.41% from 2022 to 2030 (4). The rise of the market in various regions is being driven by the increase in demand for advanced technologies in medical devices and the expansion of H-IoT in healthcare as shown in Figure 3.

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Figure 2 Revolutionary features of H-IoT in a hospital environment

Source: https://www.mdpi.com/2079-9292/12/9/2050





Source: https://www.precedenceresearch.com/internet-of-things-in-healthcare-market

2.2. Wearable and Portable electronic devices

Wearable health technology consists of the electronic devices that are worn on a person's body to send vital medical, biochemical, and exercise data to a database. Wearable technology is at the forefront of the H-IoT due to its swift adoption in smart devices and computers. Any portable devices, such as smartwatches, body patches, ear wearables, headbands, smart clothes, or smart glasses, are wearable devices. The users can use these devices to record and monitor their health data, such as the number of steps they take, how many calories they burn, their heart rate, glucose levels, stress, sugar level, etc.

From the early 21st century, wearable devices have begun to provide personalized portable devices and sensors. At present, portable devices can be classified as wrists (watches, bracelets, and gloves), heads (glasses and helmets), body clothes (coats, underwear, and pants), feet, and body sensory control devices (somatosensory modulators), as shown in Figure 4.



Figure 4 Industrial wearable technologies. (a) Evolution of wearable medical devices,(b) Application of wearable devices in healthcare and biomedical monitoring systems
At the same time, the technology mentioned above requires the use of electrical power from external sources such as batteries, which must be recharged, have a limited lifetime, and have toxicity. Which affects the environment or harms the user. As a result, efforts are being made to create environmentally friendly renewable energy sources to power these electronic devices. There are many renewable energy sources such as wind, water, solar, geothermal, biomass, and mechanical energy sources. A pulse sensor is a device that is used to monitor the heart rate or pulse of a person in real time.

Particularly in the context of wearable technology, integrating a pulse sensor with a TENG can be a valuable application (48). TENG-based self-powered medical devices are smarter, more efficient and more accurate than conventional devices, offering longer life, more effective intervention methods and more humanized data presentation (49). It can lower the financial costs and physical pain of implantable battery replacement for patients. Thus, the clinical application of TENGs is expected to be more diversified in the future, with potential applications in repairing and treating various parts, muscles, bones, and tissues (50-52), as shown in Figure 5.



Figure 5 (a) Clinical applications of triboelectric nanogenerators in nervous, cardiovascular, respiratory, and other systems. (b) Conventional medical device form factors and trends

However, the battery energy storage systems have limitations in terms of their capacity, life cycle, maintenance, and high cost (53). To overcome some of these limitations. The alternative energy storage technologies, like energy harvesting (EH) technology are being explored.

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2.3. Energy Harvesting (EH) Technology

Energy Harvesting is the process by which energy is obtained from external sources (such as renewable, water, light, heat, biomass, and mechanical energy) occurring in the immediate surroundings of the device. It is also sometimes called an energy scavenger. Unlike large-scale solar and wind installations that generate large amounts of energy, energy harvesters collect small amounts of energy from their immediate surroundings. When incorporated into mobile handsets or other small devices, they allow these devices to generate their power supply. With appropriate application of energy harvesting. Changing batteries, charging batteries, filling fuel tanks, and the like will become unnecessary. All devices will become truly wireless and independent of physical interventions. This is especially useful for devices installed in difficult to reach places. They can be operated long-term without any maintenance concerns. In addition, there are already many IoT devices in use, and the number is prospective to increase significantly in the future. Connecting each device to electricity or replacing the batteries ordinarily will become more and more difficult. Energy harvesting has the potential to eliminate those needs. Indeed, energy harvesting is a very important topic for the future of such devices, for example; hydropower (54), solar (55), wind (56), geothermal (57), biomass (58), and mechanical energy. Among the general type of EH technology, piezoelectric nanogenerators (PENGs) and triboelectric nanogenerators (TENGs) are excellent to their performance (59).

2.3.1. Triboelectric Nanogenerator (TENGs)

Nowadays, electronic devices are mostly correlated with our activities with the intention of health and communication. The most varied energy correlated with a human is mechanical energy from body motion. The triboelectric nanogenerator (TENG) was discovered by Prof. Wang and their team in 2012, Purposing at harvesting a small scale of mechanical energy. Following the electrostatic charges on the surfaces of two different tribo-materials pair when it is brought into external force, the contact induces

the triboelectric charges that can generate a potential while two surfaces are separated by mechanical force.

In 2012, Fan and team (60) reported a simple way, all polymer-based flexible generators for harvesting mechanical energy via a tribological process. By overlapping, polymer thin films of Kapton and Polyester (PET) enable electrical charge, separation, and induction processes that could be achieved through mechanical deformation of the polymer thin film. An output power density of 10.4 mW/cm³ was achieved at an output voltage of 3.3 V. This technology has great potential to power portable and personal electronic devices monitoring, as shown in Figure 6.



Figure 6 (a) The structure of an integrated generator in the bending and releasing process and related electrical measurement tests. Photographic images of a flexible TENG and mechanical bending equipment.

Zhu and their team (61) developed a new triboelectric nanogenerator in 2013, By using PDMS as a gaining electron material and Gold as a losing electron material. That could generate a maximum short-circuit current of 2 mA, and a power output of 1.2 W. The power could light up as many as 600 multicolor commercial LED bulbs, as shown in Figure 7.



Figure 7 (a) Schematic and (b) photograph of a fabricated TENG. (c) SEM image of gold nanoparticles coated on gold surface. (d and e) Footsteps fall off and on the TENG simultaneously lighting up the LEDs in real-time

That can operate an electron to flow between the two electrodes of two materials (8, 62, 63). TENG has four basic modes in detail below.

2.3.1.1. Vertical Contact Separation (VSC) Mode

The vertical contact separation mode is the simplest design of the TENG device as shown in Figure 8. This structure contains two different tribo-materials pairs and electrodes being attached on the top and bottom of the structure. Once applied the external force contacts two different tribo-materials pairs that could create oppositely charged on the surface. When the two surfaces are separated by moving out an external force. So, the two electrodes are electrically connected by a load, and free electrons in one electrode could flow to the other electrode to balance the electrostatic field. When the two electrodes are in contact again, the electron flows back (23).



Figure 8 Mechanism diagram of VSC mode

2.3.1.2. Single Electrode (SE) Mode

The single electrode mode could be freely moved that work for mobile cases as shown in Figure 9. This structure of the electrode on the bottom side is grounded. When another part (top side) is attached to the bottom side that could create an oppositely charged on surface. Once it is separated. The electrons on the surface of the material attached to the electrode flow along the external load (23).



Figure 9 Mechanism diagram of VSC mode

2.3.1.3. Lateral Sliding (LS) Mode

The lateral sliding mode is the same as the VSC mode but has a superior advantage over that mode. The structure of the lateral sliding mode as shown in Figure 10. When two different tribo-materials pairs are in contact, a relative sliding in parallel to the surface creates charges on the two surfaces. The electrons from the top and bottom sides of the electrodes could flow to the other electrode to balance the electrostatic field. So, the lateral sliding can be a planar motion, a cylindrical rotation, or disc rotation (23).



Figure 10 Mechanism diagram of LS mode

2.3.1.4. Freestanding Triboelectric Layer (FS) Mode

The freestanding triboelectric layer mode can work with a free-moving triboelectric layer between two electrodes, as shown in Figure11. When two different tribo-materials pairs are placed in parallel. The bottom material has electrodes attached and connected to an external load. When the shear force is applied, the top material moves past the first base material to the second base material. The charges of the upper material are changed with the two base materials. When the top material is separated from the base material, the electrons on the surface of the base material flow through the electrodes to an external load (23).



Figure 11 Mechanism diagram of FS mode

Furthermore, the materials that have triboelectrification effect from metal to polymer or almost every material. All of these materials can be candidate for fabricating TENG. Thus, the material choices for TENG are huge. Nevertheless, the triboelectric series is a list of materials ranked in order of their tendency to become electrically charged when they come into contact with each other through friction.

2.4. The Triboelectric series

Practically materials were known that have a triboelectrification effect. All these materials could be candidates for fabricating TENGs. Nevertheless, the ability of a material electron accepting/donating depends on its polarity (64), as shown in Figure 12. For the selection of the right triboelectric materials, strongly gaining electron materials should be paired with a strongly losing electron material from the triboelectric series. To make the suitable selection to increase the efficiency of the triboelectric effect.



Figure 12 The triboelectric series is divided from the most negative tribo-polarity to the

most positive tribo-polarity

In the literatures, almost all materials were fabricated TENG as a synthesis material. That provided a high electrical efficiency meanwhile the synthesis material is nondegradable and causes electronic waste. So, biomaterial is a good choice to replace synthesis materials because it has more advantages such as being biodegradable, biocompatible, and eco-friendly.

2.5. Biomaterials

Biomaterials are materials that are designed and engineered to interact with biological systems, such as living tissues and organisms, in a way that promotes their compatibility and functionality. Biomaterials have biocompatibility, for example; for a heart valve, or may be bioactive. Biomaterials have a wide range of applications in the fields of medicine, healthcare, and biotechnology, for example; dental applications, surgery, and drug delivery for human therapy (65). Some of the biomaterials was shown in Table 1. A milestone in green electronics is the development of materials sources. Thus, TENG devices made from biomaterials have become a practical solution for powering such implantable medical devices and health sensing purposes.

Table 1 List of biomaterials.

Biomaterials	Source/Origin	Reference
Cellulose	Wood and Cotton	(66)
Chitin	shell of Crab and Shrimp	(66)
Rice Paper (RP)	Wheat, Corn and Rice	(66)
Egg White (EW)	Egg	(66)
SF	Silk cocoon	(66)
Collagen	Animal connective tissues	(66)
Wheat Gluten	Agricultural plants	(66)
Starch	Potato, Corn, Wheat and Rice	(66)
Alginate	Algae	(66)
Gelatin	Polypeptide	(66)

In 2018, Jiang and their team (67) studied the fully bioresorbable natural-materialsbased TENGs (BN-TENGs) by using SF, RP, EW, cellulose, and chitin as tribo-material pairs. The BN-TENG was achieved the various of electrical output performance with V_{oc} of 5 to 15 V and an I_{sc} of 0.05 to 0.15 µA. The power density of 22 mW/cm² with a load resistance of about 67 mega ohms, as shown in Figure 13 and the summary of BN-TENG Table 2. The result of five biomaterials was ranked a wide range to providing a basis for materials selection and device design of the TENG.



Figure 13 (a) The natural bioresorbable polymers (NBPs) initiated from nature with wide raw material sources and (b) Open-circuit voltage (V_{oc}) and short-current (I_{sc}) of the BN-TENGs fabricated with different pairwise combinations

Tribo-positive	Tribo-negative	Output voltage	Output current	Deference
material	material	(V)	(µA)	Relefence
SF	Chitin	15	0.15	(67)
Cellulose	Chitin	13	0.10	(67)
Cellulose	RP	6	0.5	(67)
EW	SF	6	0.5	(67)

Table 2 The summary of BN-TENG

In the development of Triboelectric Nanogenerators (TENGs), energy harvesting devices that convert mechanical energy into electrical energy through the triboelectric effect, biomaterials can play an important role. Thus, the specific choice of biomaterials in TENGs will depend on the intended application of the device and the desired properties, such as biocompatibility, flexibility and efficiency of energy harvesting. The

integration of biomaterials into TENGs, particularly in areas such as wearable technology and medical devices, opens up opportunities for sustainable and biocompatible energy harvesting solutions. Among the biomaterials, SF and BC indicated the suitable choice for the tribo-material pairs for fabricating B-TENG, due to the strongest functional group of a protein family, which has a robust electron-donating tendency from $-NH_2$ and C=O group (13).

2.6. Silk

Silk is a natural protein fiber produced by insects as a material for their nests and cocoons as shown in Figure 14a. There are several types of insects that produce silk, including silkworms (the most common type of silk). The mulberry silkworm (*Bombyx mori*) belongs to the family Bombycidae as shown in Figure 14b. China is the native place of this silkworm but now it has been introduced in all the silk-producing countries like Japan, India, and Rep. Korea. Since the natural food of this worm is a mulberry leaf, it is called a mulberry silkworm. The silk produced by this moth is white as shown in Figure 14c. The *Bombyx mori* silk has been the most intensively studied.



Figure 14 (a) SEM image of silk fiber with magnification at 1000X, (b and c) Digital photo of mulberry Bombyx mori silkworm and moth

2.6.1. The structure of silk

Silk fiber mainly consists of 2 types such as sericin is a glue-like protein that contained different types of hydrophilic polar amino acids, which are 25 to 30% and fibroin is mainly contained different types of hydrophobic amino acids, which are 70 to 75%.

2.6.2. Silk Fibroin (SF)

Consists of 3 types of subunits (Figure 5a).

2.6.2.1. Heavy chain (H-chain): MW 391.6 kDa

 The hydrophobic domain such as glycine 45%, alanine 30%, serine 10%, or (G–S–G–A–G–A)_n with a repetitive hydrophobic amino acid sequence, as shown in Figure 15b.

2.6.2.2. Light chain (L-chain): MW 27.7 kDa

- The hydrophilic domain such as valine 15% with a non-repetitive amino acid sequence, as shown in Figure 15c.
- 2.6.2.3. Glycoprotein (P25): MW 25.2 kDa



Figure 15 (a) Structure of fibroin, (b and c) amino acid in fibroin

A high molecular weight protein chains have a crystalline arrangement. Which consists of highly hydrophobic amino acids for low molecular weight protein chains. The protein chains in this section are connected to the high molecular weight protein chains by disulfide bonds. So, glycoprotein (P25) provides a link between high and low molecular weight chains. The crystalline structure can be subdivided into 3 types. The silk I structure is the liquid silk fibroin stored in the glands of silkworms (pre-spun pseudo crystalline). Also known as this type of structure, random coil, or alpha-helix structure, is water soluble (unstable structure). This structure can be changed to silk II structure when heating, spinning, applying an electric field, or filling with polar solutions such as methanol or acetone. Silk structure II consists of a beta-pleated sheet structure, non-parallel linking of protein chains (anti-parallel) with hydrogen bonds between the carboxyl group and the amino group. Between the individual beta-pleated sheet overlapped by the van der Waals force, fibroin has high mechanical properties and insoluble in water (68).

2.7. SF-based TENG

SF is a protein-based biomaterial that has been explored for various applications, including its potential use in TENG. Practically all of the materials that have been examined, and their ability to gain or lose electrons has been summarized in a series of triboelectric materials (64). Interestingly, SF has a high positive level in the triboelectric series and has a strong ability to lose electrons, so many materials that easily gain electrons can be selected to form triboelectric pairs with SF to form high efficiency TENG. Hence, SF has shown promise in TENG applications, particularly in the healthcare and wearable technology sectors (69).

In 2015, Zhang and co-workers (17) developed a triboelectric nanogenerator. Which is flexible, transparent, non-toxic, and environmentally friendly. Therefore, SF is a robust electron-donating tendency of tribo-material pairs with polyethylene terephthalate (PET) as an electron-accepting material. Which is attached to indium tin oxide (ITO) as an electrode. The V_{oc} of 25.2 V, the I_{sc} of 0.25 μ A, and the P_{max} of 8.1 μ W at a load resistance of 40 mega ohms, as shown in Figure 16.



Figure 16 (a-d) Schematic of the triboelectric pairs of silk fibroin film and PET film contact each other under the external force and charges are generated, (e) Open-circuit voltage (V_{oc}) and short-current (I_{sc}) and (f) Output power of the TENG

Kim and their team (70) reported for the first time a SF nanofiber networked Silk Bio-TENG. The regenerated SF film, which is prepared by a simple electrospinning method. The electrical output was obtained with a V_{oc} and I_{sc} of 15 V and 2.5 μ A, respectively, that was higher than casting method for 2.5 times, The P_{max} of 3.75 mW/m² at load resistance of 5 mega ohms, as shown in Figure 17.



Figure 17 (a) Schematic of the triboelectric electric energy generation process. (b) Comparison of the open-circuit output voltage (V_{oc}) between electrospun and cast silk. (c) the maximum output voltage, current, and maximum power (d) of electrospun silk

Nui and their team (71) fabricated the TENG by using silk nanoribbon film (SNRF) and regenerative SF film (RSFF), which is shown outstanding output performance with a V_{oc} of about 42 V, I_{sc} of about 0.5 μ A, and a power density of around 86.7 mW/m², as shown in Figure 18.



Figure 18 (a) SNRF and (b) RSFF. (c) Schematic illustration of TENG structure. (d, e) 3D AFM images of friction layers. (f–j) Schematic diagram of TENG working principle. (k) Typical output voltage signal during one compression and release cycle

Mi *et al.* (12) was developed a high-porosity of silk-based aerogel TENG (STENG) from silk fibroin extracted from silk cocoon, exhibiting high performance and biocompatibility. The optimized STENG achieved an V_{oc} of 52.8 V and a I_{sc} of 5.2 µA. It is suitable as a power source for small electronic devices because of its high stability at different operating frequencies and over the long term, as shown in Figure 19.



Figure 19 (a) The open-circuit output voltage (V_{oc}), (b) the short-circuit current (I_{sc}) of silk-based aerogel TENG (STENG) and (c) schematic of STENG device

Tribo-positive	Tribo-negative	Output voltage	Output current	Poforonco
material	material	(V)	(µA)	Reference
SF film	ITO	25	0.25	(17)
SF film	PI	8	1	(70)
SF electrospun	PI	15	2.5	(70)
RSFF	SNRF	42	0.5	(71)
SF film	PTFE	16	2	(12)
SF aerogel	PTFE	52.8	5.2	(12)

Table 3 The summary of SF-based TENG were reported

2.8. Bacterial Cellulose (BC)

Cellulose is a natural polysaccharide, or long-chain carbohydrate, which is an essential structural component of the cell walls of plants and certain algae, called plant cellulose (PC). Cellulose is one of the most common organic compounds on earth and has several important functions in nature (72). The purest form of cellulose known as bacterial cellulose (BC), that is a unique form of cellulose. The cellulose and BC are both forms of cellulose, which is a natural polymer made up of repeating glucose molecules linked together by beta-1,4-glycosidic bonds as shown in Figure 20.

However, they differ in their properties (73-78), as shown in Table 3. BC was produced by certain strains of bacteria from *Acetobacter* genus, for example; *A. xylinum, A. hansenii, and A. plateurianus* (75). To summarize, cellulose is a naturally occurring polymer found in plant cell walls and certain algae, while bacterial cellulose is produced by certain bacteria. Although they are both made up of glucose molecules linked together by beta-1,4-glycosidic linkages, they have different structures and properties that make bacterial cellulose particularly suitable for certain applications, including those in the healthcare and biotechnology sectors (79).



Table 4 Comparison of properties for PC and BC

Properties	PC	BC	Reference
Tensile strength (MPa)	25 to 200	20 to 300	(73)
Young's modulus (MPa)	Sheet: 0.2 to 2.5	20000	(74)
Size fiber (nm)	Micron scale	20 to 100	(77)
Crystallinity (%)	40 to 85	74 to 96	(78)
Purity (%)	< 80	> 99	(75)

2.9. BC-based TENG

Bacterial cellulose (BC) is a natural biomaterial. It has gained attention in the development of triboelectric nanogenerator (TENG) and related energy harvesting devices. There are several advantages and unique properties of BC-based TENG.

Kim and his team (20) was reported the development of a bacterial nanocellulosebased bio triboelectric nanogenerator (BNC Bio-TENG) with unique functionalities including transparency, flexibility, and biocompatibility. The electrical output performance of V_{oc} and I_{sc} of 13 V and 11 µA, respectively. The P_{max} of 4.8 mW/m² at load resistance of 1 mega ohm, as shown in Figure 21.



Figure 21 (a) Schematic of BNC Bio-TENG with arc-shape structure, (b) output voltage and current of BNC Bio-TENG, (c) power density at different load resistance (ohm)

Shao and their team (21) was studied the fabrication of an environmentally friendly triboelectric nanogenerator (TENG) based on a bacterial cellulose (BC) film by means of a vacuum filtration method. The electrical output of V_{oc} and I_{sc} of 120 V and 10 μ A, respectively, as shown in Figure 22. The TENG demonstrated excellent stability. It also demonstrated the ability to harvest mechanical energy from human movement.



Figure 22 (a) short-circuit current, (b) open-circuit output voltage of pure BC-TENG and (c) SEM image of pure BC film

Jakmuangpak *et al.* (19) was fabricated bio-TENGs using bacterial cellulose (BC) films. The BC film enhanced the triboelectric signals, resulting in a TENG with a maximum voltage and current of 25 V and 2.2 μ A, respectively, as shown in Figure 23.



Figure 23 (a) open-circuit output voltage, (b) short-circuit current of pure BC-TENG and (c) SEM image of pure BC film

Zhang *et al.* (80) was demonstrated BC-TENG exhibited a V_{oc} of 19 V, I_{sc} of 0.3 mA, respectively, as shown in Figure 24. The BC TENG with a portable electronic device allowed for the collection of mechanical energy through human-machine movement, showcasing the potential of cellulose-based materials in TENG and other electronic applications



Figure 24 (a) open-circuit output voltage, (b) short-circuit current of pure BC-TENG at various size and (c) SEM image of pure BC film

Shen *et al.* (22) was fabricated the pure BC TENG with low cost, self-supplying, and the ability to use low-frequency motion for effective operation. The BC TENG provided a I_{sc} of 4 µA, V_{oc} of 55 V, as shown in Figure 25. Overall, the results demonstrate the successful fabrication of an all-cellulose TENG with good performance and biodegradability. This makes it suitable for eco-friendly electronics and wearable self-powered interfaces



Figure 25 (a) open-circuit output voltage, (b) short-circuit current of pure BC-TENG at various size and (c) SEM image of pure BC film with different magnification

Tribo-positive	Tribo-negative	Output voltage	Output current	Deference
material	material	(V)	(µA)	Relefence
Cu	BC film	13	11	(20)
BC film	PDMS	120	10	(21)
BC film	ITO	25	2.2	(19)
BC film	BC/Ppy	19	0.3	(80)
BC film	PDMS	55	4	(22)

Table 5 The summary of BC-based TENG were reported

Due to biomaterials having inconspicuous electrical properties. That makes it difficult to produce electronic devices from biomaterials to achieve high efficiency. Therefore, the material improves electrical performance by making composite materials with the addition of a diffusion phase. So, the filler material can be divided into two major categories: conductor and insulator. The addition of a conductor or conductive material to increase the charge transfer capacity. The most popular is to fill insulators, including dielectric, piezoelectric, and ferroelectric to increase the ability to generate charge or increase the charge density. To accomplish this, searching for increasing the efficiency of the charge generating layer through chemical and physical methods by material selection (25). The composite material fabrication and structural design (28) is now interesting. So far, compositing is the most common method that used for enhancement of charge generating layer by adding fillers.

2.10. Composite materials

A composite material is made by combining two or more natural or artificial materials with the resultant material having better properties than the two materials alone (81). There are two constituent parts to a composite material, the reinforcements, and the matrix. The new material is usually noted for being stronger, lighter, and less expensive than traditional materials.

Composites are regularly classified by the type of material used for the matrix. The four primary categories of composites are polymer matrix composites (PMCs), metal matrix composites (MMCs), ceramic matrix composites (CMCs), and carbon matrix composites (CAMCs). So, carbon-carbon composites (CCCs) are the most important subclass of CAMCs. Now, PMCs are by far the most popularly used type of composite. Although, there are important applications of the other types which are indicative of their great potential in mechanical engineering applications.



Figure 26 Types of Composite materials

2.10.1. Matrix

The continuous phase is also known as the matrix, which is ordinarily a polymer, a metal, or a ceramic, for example; polymers have low strength and stiffness, metals have intermediate strength and stiffness but can have high ductility, whilst ceramics have high strength and stiffness but will also be more brittle. So, the matrix can be divided into two types, organic and inorganic. Organic matrices such as polymers are very common (especially for fiber-reinforced plastics) and are typically used to create composites containing fiberglass, carbon fiber, or aramid fiber. While inorganic matrices are often employed in concrete, metals, ceramics, and glasses.

2.10.1.1. Polymer Matrix Composite (PMCs)

Polymer matrices usually are relatively weak, low-stiffness, viscoelastic materials. The strength and stiffness of PMCs come mostly from the reinforcing fibers. There are two major classes of polymers used as matrix materials, thermosets, and thermoplastics. At this time, thermosets are by far the most widely used matrix resins for structural applications. Thermosets tend to be more resistant to solvents and corrosive environments than thermoplastics. Thermosets are materials that undergo a curing process during part fabrication, after which they are rigid and cannot be reformed. On the other hand, thermoplastics can be repeatedly softened and re-formed by the application of heat.

2.10.1.2. Metal Matrix Composite (MMCs)

Metal matrix composites (MMCs) normally include a low-density metal, such as aluminum or magnesium, reinforced with particulate or fibers of a ceramic material, such as silicon carbide or graphite. Compared with unreinforced metals, MMCs offer higher specific strength and stiffness, higher performing temperature, and greater wear resistance, as well as the opportunity to tailor these properties for a specific application.

2.10.1.3. Ceramics Matrix Composite (CMCs)

The CMC matrices are silicon carbide, alumina, silicon nitride, mullite, and various types of cement. The properties of ceramics, especially strength, are even more process sensitive than those of metals. The ceramics are very flaw sensitive, resulting in a decrease in strength with increasing material volume, a phenomenon called the size effect. As a result, there is no single value that describes the tensile strength of ceramics. In fact, because of the very brittle nature of ceramics, it is difficult to measure tensile strength, and flexural strength (modulus of rupture). Because of the major difficulty in measuring a simple property like tensile strength, which emerges from their flaw sensitivity, it is not surprising that ceramics are rarely used in applications where they are subjected to significant tensile strengses.

2.10.1.4. Carbon Matrix Composite (CAMCs)

Carbon is a remarkable material. It consists of materials from lubricants to diamonds to structural fibers. The forms of carbon matrices resulting from the various carbon–carbon manufacturing processes tend to be rather weak, brittle materials. Thermal conductivities are from very low to high, depending on precursor materials and processes. As for ceramics, in situ matrix properties are difficult to measure.

2.10.2. Reinforcement

The four types of reinforcements (82)used in composites are continuous fibers, discontinuous fibers, whiskers (elongated single crystals), and particles, as shown in Figure 27. Continuous, aligned fibers are the most efficient reinforcement form and are widely used, especially in high-performance applications. However, for ease of fabrication and to achieve specific properties, such as improved impact resistance, continuous fibers are converted into a wide variety of reinforcement forms using textile technology.



Figure 27 Reinforcement forms

2.10.2.1. Fiber-reinforced

Fiber-reinforced composite materials include fibers of high strength and modulus embedded in or bonded to a matrix with distinct interfaces (boundaries) between them. Both fibers and matrix conserve their physical and chemical identities, they produce a combination of properties that cannot be attained with either of the compositions acting alone. In general, fibers are the essential load-carrying members, as the surrounding matrix keeps them in the desired location and orientation acts as a load transfer medium between them and protects them from environmental damages due to raised temperatures and humidity (83).

2.10.2.2. Particle-reinforced

The large-particle and dispersion-strengthened composites are the two subclassifications of particle-reinforced composites. The difference between these is based on reinforcement or strengthening mechanisms. In essence, the matrix transfers some of the applied stress to the particles, which bear a fraction of the load. For dispersion-strengthened composites, particles are normally much smaller, with diameters between 0.01 and 0.1 mm (10 and 100 nm). Whereas the matrix carries the major section of an applied load, the small-dispersed particles obstruct or impede the motion of dislocations. Thus, plastic deformation is limited such that yield and tensile strengths, as well as hardness, improve (83).

2.10.2.3. Structural

A structural composite is regularly composed of both homogeneous and composite materials, the properties of which depend not only on the properties of the composition materials but also on the geometrical design of the various structural elements. Laminar composites and sandwich panels are two of the most common structural composites. A laminar composite is composed of two-dimensional (2D) sheets that have a preferred high-strength direction such as continuous and aligned fiberreinforced plastics. The layers are stacked together so that the orientation of the highstrength direction varies with each connected layer, as shown in Figure 28. Sandwich panels, regarded to be a class of structural composites, are designed to be lightweight or panels having relatively high stiffnesses and strengths. A sandwich panel encloses two outer sheets or faces, that are split by an adhesively bonded to a thicker core, as shown in Figure 29. (83)

•••••



Figure 28 The stacking of respective oriented, fiber-reinforced layers for a laminar

composite



Figure 29 Diagram showing the construction of a honeycomb core sandwich panel

Searching for effective strategies for increasing the efficiency of TENG through chemical and physical methods by material selection, surface modification, and structural design is now interesting. Improving the electrical efficiency of natural-based friction materials by making composite material *via* adding a dispersion phase of dielectric, piezoelectric, and/or ferroelectric (84).

2.11. Dielectric materials

Dielectric materials are insulators. They do not have any loosely bound or free electrons that may drift through the material. Thus, dielectric materials support dielectric polarization, which enables them to act as dielectrics rather than conductors. This phenomenon occurs when a dielectric is placed in an electric field and positive charges are displaced in the direction of the electric field. While the negative charges are displaced in the opposite direction. The polarization creates a strong internal field, which reduces the overall electric field within the material. That is an important material for making a capacitor.



Figure 30 Dielectric material

2.12. Dielectric nanomaterials

A nanometer is one-millionth of a millimeter, approximately 100,000 times smaller than the diameter of a human hair. Nano-sized particles are contained in nature and can be created from a variety of products, such as carbon or minerals like silver, but nanomaterials must have at least one dimension that is less than approximately 100 nanometers. They have separated into three groups such as zero, one, two, and threedimensional (not the nanomaterials except nanocomposite) nanostructure, as shown in Figure 31.

2.12.1. Zero-Dimensional (0D) nanostructure

In zero-dimensional nanomaterials (0D), all the dimensions are measured within the nanoscale (no dimensions are larger than 100 nm) (85). Most regularly, 0D nanomaterials are nanoparticles, for example; fullerene or C_{60} , and quantum dot.

2.12.2. One-Dimensional (1D) nanostructure

In one-dimensional nanomaterials (1D), one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires.

2.12.3. Two-Dimensional (2D) nanostructure

In two-dimensional nanomaterials (2D), two dimensions are outside the nanoscale. This class exhibits plate-like shapes and includes graphene, nanofilms, nanolayers, and nanocoating.


Figure 31 Classification of nanoscale dimension

In the context of a Triboelectric Nanogenerator (TENG), an energy harvesting device, dielectric materials are commonly used to improve generator performance. To enhance the triboelectric effect and overall energy conversion efficiency, these dielectric materials are often integrated or composited with other materials.

In 2020, Saichon et al. (32) developed of lightweight, and flexible high-performance TENG with incorporating dielectric $Ti_{0.8}O_2$ nanosheet in cellulose filter paper (CFP) as the friction layer. The modified CFP-based TENG demonstrates an V_{oc} and current density of 42 V and 1 μ A/cm², respectively, with a power density of 25 μ W/cm². The electrical output performance was higher than the unincorporating filler in TENG device. It was powered of lighting up LED bulbs, charging capacitors, and detecting simple human motions, as shown in Figure 32.



Figure 32 (a) Optical images of the modified CFP without, (b) with contained of $Ti_{0.8}O_2$ NS, (c) output voltage, and (d) output current density of the modified CFP-TENG

In 2023, Saichon et al. (86) was demonstrated the enhancement of bacterial cellulose (BC)-based triboelectric nanogenerator (TENG) performance by incorporating Ti_2NbO_7 nanosheets (NS). The addition of 5% (v/v) Ti_2NbO_7 NS into the BC film improved the electrical outputs of TENG, with voltage and current values approximately 25 V and 5 μ A, respectively, that higher than 2 to 4 times of pure BC, as shown in Figure 33.



Figure 33 (a) SEM image of pure BC, (b) BC/Ti₂NbO₇ composite film, (c) output voltage, and (d) output current of the modified BC-TENG

2.13. 2D nanosheet materials based on TENG

The choice of triboelectric material is crucial for TENG. 2D materials, for example; transition metal dichalcogenides (TMDs), hexagonal boron nitride (h-BN), MXenes, and layered double hydroxide (LDH), are well suited for TENG applications due to advantages such as excellent electrical properties, transparency, flexibility and high surface area (87). The TMDs, h-BN, and MXene has main limitation, such as expensive with sophisticated instruments, time-consuming, complicated procedures, in addition with highly trained technicians to perform. Thus, LDH was a simple synthesized *via* co-precipitation method between divalent metal cation/trivalent metal cation (M²⁺/M³⁺) that is feasible on laboratory and industrial scales (88).

2.14. Layered Double Hydroxide (LDH)

Single-layer nanosheets have found widespread application in various fields, including electronics (59), and dielectric material (89). Layered double hydroxides (LDH) are 2D, hydrotalcite $[Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O]$ like basic inorganic compounds (90). They are demonstrated by the general formula,

$$\left[\mathsf{M}^{2^{+}}_{(1-x)} \mathsf{M}^{3^{+}}_{x} (\mathsf{OH})_{2}\right]^{x^{+}} (\mathsf{A}^{n^{-}}_{x/n}) \bullet \mathsf{mH}_{2}\mathsf{O}$$

Where;

M²⁺= divalent metal cation.

 M^{3+} = trivalent metal cation.

 $x = an integer = M^{3+}/(M^{2+}+M^{3+}) = molar fraction.$

Aⁿ⁻ = organic or inorganic charge compensating anion in the inter-lamellar region.

m = the number of water molecules present per formula weight of a compound.

The ordinary structural scheme of LDH is demonstrated in Figure 34. According to the general formula and the structural diagram, these compounds require positively charged hydroxylated layers $[M^{2+}_{(1-x)} M^{3+}_{x} (OH)_{2}]^{x+}$ separated by interlayered anionic species $(A^{n-}_{x/n}) \cdot mH_{2}O$ and water molecules (91). Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , etc., and Al^{3+} , Cr^{3+} , Fe^{3+} , V^{3+} , Co^{3+} , etc. are M^{2+} and M^{3+} normally indicate in basic layers of these compounds. In the meantime, CO_{3}^{2-} , SO_{4}^{2-} , Cl^{-} , NO^{3-} , OH^{-} etc. are charge-compensating anions indicate in the interlayer space between two respective layers (92). So, *x* is the number of moles of M^{3+} per formula weight of the compound which is the sum of that of M^{2+} and M^{3+} . It imposes the charge density of the hydroxide layers of these compounds, the range between 0.2 to 0.4 according to the stoichiometry of the compounds.



Figure 34 Structure diagrams for LDHs $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_{2}]^{x+}(A^{n-}_{x/n}) \cdot mH_{2}O$

Yu and co-workers (88) reported the simple one-step process offered significant savings in cost and time. In the 10 minutes process outlined here to synthesize LDH single-layer nanosheets by the co-precipitating method of Mg²⁺ and Al³⁺. Thus, this new approach is promising for the large-scale synthesis of single-layer nanosheets for various applications, as shown in Figure 35.



Figure 35 Structure of (a) 3D structure and (b) TEM image of MgAI LDHs

Lahkale and their team (93) examined the effect of aluminum content on optical, electrical and dielectric properties of mixed metal oxides (MMOs). Whereas lower aluminum content (or increasing Mg/Al molar ratio (R)) showed lower values of conductivity, dielectric constant and dielectric loss tangent, which promises an interesting dielectric application for MMOs, as shown in Figure 36.





(d) Dielectric loss tangent as a function of R

Cui et al. (42) was introduced a bottom-up approach to fabricate meter-scale of the modified TENG by growing layer double hydroxide nanosheets (LDH NS) on a metal substrate. The modified TENG could generate higher the V_{oc} , and the current density of 13 V, and 1.6 μ A/cm² compared to the unmodified TENG, as shown in Figure. Nevertheless, MgAl LDH can be candidate to improvement the electrical output performance by filling in charge generating layer for TENG.



Figure 37 (a) Digital image of pristine Al foil substrate (top) and modified LDH NS on Al foil substrate (bottom), (b) SEM image of modified LDH NS at six random locations, (c) output voltage and (d) current density of modified TENG

However, when the charge generated on the contact layer is only a temporary charge. Therefore, to solve these problems this research is interested in increasing the charge density of the material and designing the structure of the TENG as a multilayer structure.

2.15. Material approaches to enhance the triboelectric power

The material aspects for the enhancement of the electrical power output are discussed, and then the material designs are discussed. This report concludes with future challenges and proposed materials in TENG (43).

2.15.1. Charge trapping layer

The charge-trapping layer plays a crucial role in blocking the combination of surface charges, which can interfere with surface charge accumulation and cause a decrease in the triboelectric potential (46). Recent, studies have reported that polymers containing aromatic rings in their chains, such as polystyrene (PS) and polyimide (PI), have many trapping sites due to the nonuniform energy levels along their main chains (94).

Cui et al. (44) focused on improving the output performance of triboelectric nanogenerators (TENGs) by increasing the triboelectric charge density on the friction layer. The TENG was inserted charge trapping layer consisting of polystyrene (PS) between polyvinylidene fluoride (PVDF) and electrode is fabricated and tested. It was shown a significant increase in triboelectric charge density higher charge density than TENG without charge trapping layer for 7 times, as shown in Figure 38.



Figure 38 (a) Charge density of PS/PVDF multilayer structural

Cui et al. (45) developed the triboelectric nanogenerators (TENGs) by increasing the triboelectric charge density on the friction layer. The TENG was inserted charge trapping layer consisting of polystyrene (PS) between polyvinylidene fluoride (PVDF) and electrode is investigated. It was shown a charge density higher than device A and B for 2.1 times. The result was demonstrated the effectiveness of the PS/PVA approach in enhancing the charge capacity and overall performance of TENG, as shown in Figure 39.



Figure 39 (a) Schematic of PS/PVA TENG, (b) charge density of device samples and (c) current of devices

2.16. Lignin

Lignin is a complex and heterogeneous polymer with a highly variable aromatic compounds and structure (95). Its exact composition and structure can vary depending on the plant species, tissue type, and the extraction or isolation method used (96). The composition and content of lignin is dependent on the environment and the species of the plant. In hardwood lignin, "S" and "G" are the main units, with minor "H" units present, while in softwood lignin, "G" units are mainly present with minor "H" units as shown in Figure 40.



Figure 40 Basic structural unit of lignin

2.16.1. Different lignin types based on extraction technique

Lignin can be obtained from a variety of sources and has different chemical structures and compositions with different properties (97). There are two major types of lignin based on extraction processes, sulfur lignin and sulfur-free lignin (98). Sulfur-containing lignin, such as *kraft lignin* and *lignosulfonates*, is a byproduct of commercial chemical pulping processes used in the paper and pulp industries. These processes involve the use of sulfur-based chemicals. On the other hand, sulfur-free lignin, which includes *soda or alkaline lignin* and *organosolv lignin*, is produced as a byproduct of bioethanol production processes. These bioethanol processes do not involve sulfur-based chemicals (99, 100) as shown in Figure 41.



Figure 41 Structural characteristic of kraft pine lignin (A) and lignosulfonate lignin (B)

CHAPTER 3 RESEARCH METHODOLOGY

This research fabricated the flexible materials-based composite multilayer triboelectric nanogenerator (F-TENG) by using silk fibroin and bacterial cellulose composite as the primary and secondary friction material. The preparation process is divided into step by step, including the preparation of Silk Fibroin extraction, the preparation of Bacterial cellulose slurry, the synthesis of MgAI LDH NS, the preparation of bio-material composites, and the fabrication of F-TENG.

3.1. Chemicals, Materials, and Equipment for Silk fibroin (SF) solution

- 3.1.1. Chemicals
 - Bombyx mori Silk cocoons, Buriram province, Thailand
 - Sodium carbonate (Na₂CO₃), Sigma-Aldrich
 - Silver nitrate (AgNO₃), Sigma-Aldrich
 - Calcium chloride (CaCl₂), Sigma-Aldrich
 - Ethanol (C₂H₅OH) 95%, AR Lab ••••••
 - Deionized water
 - Glycerol (C₃H₈O₃) 99.5%, Carbo Erba Reagent Germany
 - Polyethylene glycol (PEG-400), Krungthepchemi

3.1.2. Materials and Equipment

- Beaker (50, 250, 800, and 4000 mL)
- Cylinder glass (200 mL)
- Pipette (10 mL)
- Centrifuge tube (50 mL)
- Thermometer (-2 to 100°C)

- Glass rod
- Forceps
- Spatula
- Weighting boat
- Mold (8.5*9.5 cm²)
- Dialysis tubing/ Cellulose membrane (14 kDa MW), Sigma-Aldrich
- Magnetic bar
- Hotplate stirrer
- Analytical balances, METTLER TOLEDO model PL1502-S
- Hot air oven
- pH meter, Metrohm Siam Ltd., 827 pH Lab

3.1.3. Preparation of Silk fibroin (SF) solution

First, 20 g of *Bombyx mori* Silk cocoons were de-sized finely and boiled in an aqueous solution of 0.048 M sodium carbonate at 75°C for 1 hour with continuous stirring to remove the sericin. The treated silk fibers were rinsed in deionized (DI) water more than three times to remove sericin residue. The dried silk fibers were squeezed out of excess water and dried in the hot air oven at 50°C overnight, Figure 42. Second, Ajisawa's solution was prepared by dissolving calcium chloride with ethanol and DI water (1:2:8 molar proportion), then dried silk fibers were added into Ajisawa's solution at 75°C for 2 hours with continuous stirring and centrifuge at 8000 rpm, 4°C for 30 minutes to remove impurity (Undissolved silk), Figure 43. Finally, the silk/Ajisawa's solution mixture is poured into a 14 kDa MW dialysis bag, dialyzed against DI water at 4°C until CaCl₂ ions disappear by testing with silver nitrate, and then centrifuged at 8000 rpm for 30 minutes to remove impurities and kept SF solution at 4°C before use, Figure 44.



Figure 43 Preparation of Ajisawa's solution and Dissolving process



Soak in DI water at 4°C and stir continuously

Drop $AgNO_3$ solution to test Cl⁻ in SF solution



Silk Fibroin solution centrifuge at 8000 rpm, 4°C for 30 minutes and keep at 4°C before use

Figure 44 Desalting process (Dialysis process)

3.1.4. Fabrication of Silk fibroin (SF) film

The SF solution was mixed with glycerin and PEG-400 by stirring continuously for 10 minutes. Then pour the mixed SF solution into a mold and dried in the hot air oven at 45°C overnight as shown in Figure 45.



Figure 45 Fabrication of SF film

3.2. Chemicals, Materials, and Equipment for Bacterial Cellulose (BC) slurry

- 3.2.1. Chemicals
 - Nata de Coco
 - Benedict's Solution
 - Deionized water

3.2.2. Materials and Equipment

- Beaker (250, 500, and 1000 mL)
- Conical Flask (250 mL)
- Test tube
- Cylinder (200 mL)
- Blender
- Magnetic bar
- Hot plate stirrer
- Analytical balances, METTLER TOLEDO model PL1502-S
- Hot air oven

3.2.3. Preparation of Bacterial Cellulose (BC) slurry

First, the de-sugaring process of commercial Nata de Coco was washed twice, de-sized, and boiled at 80°C for 30 minutes. Sugar testing was tested by using Benedict's solution boiled at 100°C for 5 minutes (repeat until the color of the solution did not change). Finally, the Nata de Coco was finely blended to obtain the BC slurry, which was stored at 4°C before use, Figure 46.



Figure 46 Preparation of Bacterial Cellulose (BC) slurry

3.2.4. Fabrication of Bacterial Cellulose (BC) film

The BC slurry was mixed with glycerin by stirring continuously for 10 minutes at 65°C to degases. Then pour the slurry into a mold and dried in the hot air oven at 50°C overnight, Figure 47.



Figure 47 Preparation of Bacterial Cellulose (BC) film

3.3. Chemicals, Materials, and Equipment for MgAI LDH NS

3.3.1. Chemicals

- Magnesium nitrate hexahydrate (Mg(NO₃)₂•6H₂O) 99%, Fluka Analytical
- Aluminum nitrate nonahydrate (Al(NO₃)₃•9H₂O) 98%, Kanto chemical
- Sodium nitrate (NaNO₃) 99%, Lobachemie
- Sodium hydroxide (NaOH) 98%, Carlo Erba Reagent Germany
- Formamide 99.8%, Sigma-Aldrich
- Deionized water

3.3.2. Materials and Equipment

- Beaker (150, 500, 800 mL)
- Volumetric flask (500 mL)
- Duran bottle (500 mL)
- Burette (50 mL)
- Cylinder glass (50 mL)
- Centrifuge tube (50 mL)
- Thermometer (-2 to 100°C)
- Glass rod
- Spatula
- Magnetic bar
- Hot plate stirrer
- Analytical balances, METTLER TOLEDO model PL1502-S
- pH meter, Metrohm Siam Ltd., 827 pH Lab

3.3.3. Preparation of MgAI LDH NS

First, prepare the magnesium nitrate hexahydrate (0.04 M), aluminum nitrate nonahydrate (0.01 M), sodium nitrate (0.01 M), and sodium hydroxide (0.25 M) by dissolving in deionized (DI) water. Then mix the 23 vol% of formamide in sodium nitrate

at 80°C and adjust the pH 10 (as solution A). Drop the magnesium nitrate hexahydrate and aluminum nitrate nonahydrate 100 mL into solution A and stir for 30 minutes. Centrifuge at 8000 rpm for 10 minutes and wash with DI water, repeat this process three times. Finally, adjust the volume to 250 mL and store it at room temperature, Figure 48.



3.4. Chemicals, Materials, and Equipment for Biomaterial (SF and BC) composite films

- 3.4.1. Chemicals
 - SF solution
 - BC slurry
 - MgAI LDH NS colloidal
 - Lignin powder
 - Glycerol (C₃H₈O₃) 99.5%, Carbo Erba Reagent Germany
 - Polyethylene glycol (PEG-400), Krungthepchemi

3.4.2. Materials and Equipment

- Beaker (50 and 250 mL)
- Dropper
- Thermometer (-2 to 100°C)

- Mold $(8.5*9.5 \text{ cm}^2)$
- Tray
- Magnetic bar
- Hotplate stirrer
- Hot air oven

3.4.3. Fabrication of Biomaterial (SF and BC) composite films

3.4.3.1. Fabrication of SF/MgAI LDH NS

The SF solution was mixed with glycerin, PEG-400, and MgAl LDH NS colloidal at 0.5, 1, 1.5, 3, 6 and 12%(v/v) by stirring continuously for 10 minutes. Then pour the mixed solution into a mold and dried in the hot air oven at 45° C overnight, Figure 49.



Figure 49 Fabrication of SF/MgAI LDH NS

3.4.3.2. Fabrication of BC/MgAI LDH NS

The BC slurry was mixed with glycerin and MgAl LDH NS colloidal at 0.25, 0.5, 1, 1.5, 3, and 6%(v/v) by stirring continuously for 10 minutes at 65° C. Then pour the mixed slurry into a mold and dry in the hot air oven at 50° C overnight, Figure 50.



Figure 50 Fabrication of BC/MgAI LDH NS

3.4.3.3. Fabrication of SF/Lignin

The SF solution was mixed with glycerin, PEG-400, and Lignin powder at 0.25, 0.5, 1, and 1.5%(w/v) by stirring continuously for 10 minutes. Then pour the mixed solution into a mold and dried in the hot air oven at 45° C overnight, Figure 51.



Figure 51 Fabrication of SF/Lignin

3.4.3.4. Fabrication of BC/Lignin

The BC slurry was mixed with glycerin and Lignin powder at 0.25, 0.5, 1, and 1.5%(w/v) by stirring continuously for 10 minutes at 65°C. Then pour the mixed solution into a mold and dried in the hot air oven at 50°C overnight, Figure 52.



Figure 52 Fabrication of BC/Lignin

3.5. Fabrication of Bio-Based composite flexible multilayer triboelectric nanogenerator (F-TENG)

The F-TENG in this research was fabricated in the form of a Vertical Contact-Separation mode (VCS mode). The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribo-material pair movement during the VCS process. The Biomaterials composite films were cut into $3 \times 3 \text{ cm}^2$, and the AI tape was used as an electrode with Cu wire connections, Figure 51.



Figure 53 Fabrication of the Bio-Based composite flexible multilayer triboelectric nanogenerator (F-TENG)

3.6. Characterization technique

Morphological, functional group and chemical structures were characterized using various techniques and electrical output efficiencies were determined.

3.6.1. Structural and functional group inspection with Attenuated Total Reflectance Fourier transform Infrared (ATR-FTIR) technique

The functional groups of the SF film, SF composite films, BC film, and BC composite films were investigated using Attenuated Total Reflectance Fourier transform Infrared (ATR-FT-IR) spectroscopy (Thermo Scientific, Nicolet 6700, US). Samples were cut into the size of $1 \times 1 \text{ cm}^2$ before analyzing the functional groups within a wavenumber range of 4000 to 550 cm⁻¹.



Figure 54 Attenuated Total Reflectance Fourier transform Infrared (ATR-FT-IR) spectroscopy

3.6.1. Structural and functional group inspection Raman spectroscopy technique

The molecules of SF film, SF composite films, BC film, and BC composite films were identified to confirm the existence of the composite and the fingerprint of SF film, SF composite films, BC film, and BC composite films by using Raman spectroscopy (Raman) as shown in Figure 47 and the samples were prepared in 1x1 cm². The results of Raman showed a strong symmetry molecular vibrational while ATR-FTIR shown an asymmetry molecular vibrational.



Figure 55 Raman spectroscopy

3.6.2. Morphological study by the scanning electron microscope (SEM)

A scanning electron microscope (SEM) (FEI, Quanta 250, USA) was used to observe the surface morphology of the samples. The sample stub was rubbed with sandpaper to remove rust and impurity. The samples of SF film, SF composite films, BC film, and BC composite films were cut into $1 \times 1 \text{ cm}^2$ and attached to the stub. The samples were gold-coated for 90 seconds before imaging with the SEM to improve their conductivity.



Figure 56 The scanning electron microscope (SEM)

3.6.3. Ultraviolet-visible (UV-Vis) spectrophotometer

Ultraviolet-visible (UV-Vis) spectrophotometers use a light source to illuminate a sample with light across the UV to the visible wavelength range (typically 190 to 900 nm). The sample was prepared 0.1 mL and dilute with DI water in a 100 mL volumetric flask. The sample was poured in a quartz cuvette 3/4 of the volume and analyzed to determine the substances.



Figure 57 Ultraviolet-visible (UV-Vis) spectrophotometers

3.6.4. X-ray diffraction (XRD)

X-ray diffraction is a common technique that determine a sample's composition or crystalline structure. The samples of SF film, SF composite films, BC film, and BC composite films were cut into $3 \times 3 \text{ cm}^2$ and the finely ground sample powder is filled onto the sample holder.



Figure 58 X-ray diffraction (XRD)

3.6.5. Synchrotron Radiation X-ray Tomographic Microscopy (SR-XTM)

Synchrotron Radiation X-ray Tomographic Microscopy is a non-destructive visualization technique, which reveals the microstructure inside opaque sample without thin sectioning. Then 3D structure is reconstructed from X-ray projections. Image contrast is based on differential X-ray absorptions inside that are varied by mass attenuation, thickness, and density.



Figure 59 Synchrotron Radiation X-ray Tomographic Microscopy (SR-XTM)

3.7. Electrical measurement of TENG device

3.7.1. Oscilloscope

Oscilloscopes (or scopes) test and display voltage signals as waveforms, visual representations of the variation of voltage over time. The signals are plotted on a graph, which shows how the signal changes. The vertical (Y) access represents the voltage measurement and the horizontal (X) axis represents time.



Figure 60 Oscilloscopes

3.7.2. Digital Multimeter

A digital multimeter is a device for measuring various electrical characteristics. A multimeter can be used to measure DC voltages and currents, AC voltages and currents, frequencies, capacities, resistances or temperatures. A test for the operation of transistors, diodes, or the electrical continuity can also be performed with the device.



Figure 61 Digital multimeter

CHAPTER 4 RESULTS AND DISCUSSIONS

In this work, the structural design of a multilayer TENG (M-TENG) based on biobased composites as a main friction layer is categorized into two systems, consisting of SF-based M-TENG and BC-based M-TENG. The single layer TENG (S-TENG) was fabricated firstly by using SF and BC as charge generating layer for each system. Herein, the MgAI LDH was added into the SF and BC to improve the electrical output performance before designing multilayer structure. After the optimum condition was found, the multilayer structure was designed by inserting SF/lignin film (SF-based/M-TENG) and BC/lignin film (BC-based/M-TENG) between charge generating layer and its electrode. The intermediate SF/lignin or BC/lignin were called a charge trapping layer.

In this chapter, the results and discussions are started with the MgAI LDH NS characterization, followed by SF/MgAI LDH (S-TENG and M-TENG), and BC/MgAI LDH (S-TENG and M-TENG). For each composite system, the physical properties, surface morphology, and chemical structure characterization are explained and discussed. The electrical output is reported with the presence of practical applications for real-time driving of the LEDs and portable devices i.e., digital watch and portable light. In addition, there are not only discusses the experimental results, but also discusses the scientific understanding of the working mechanism.

4.1. Magnesium Aluminum Layer double hydroxide nanosheets (MgAI LDH NS)

4.1.1. The synthesis and characterization of MgAI LDH NS

Various techniques were used to characterize MgAl LDH. The morphology of MgAl LDH NS was examined by digital imaging and SEM techniques. ATR-IR and XRD were used for chemical structural characterization and phase identification.

4.1.1.1. The synthesis of MgAI LDH NS

The rapid synthesis (10 min) of MgAI LDH NS with a theoretical chemical formula of $[Mg_{0.8}AI_{0.2}(OH)_2] [(NO_3)_{0.2}]_{(s)}$ was performed directly as explained earlier in experimental part (101) by following to the chemical reaction (1) and (2).

 $\begin{array}{l} 0.8Mg(NO_3)_2 \cdot 6H_2O_{(aq)} + \ 0.2Al(NO_3)_3 \cdot 9H_2O_{(aq)} + \ 2NaOH_{(aq)} \\ \rightarrow Mg_{0.8}Al_{0.2}(OH)_2(NO_3)_{0.2\,(s)} \cdot 15H_2O_{(l)} + \ 3NaNO_{3\,(aq)} \end{array}$

Equation 1 The chemical reaction of MgAI LDH synthesis

 $Mg_{0.8}Al_{0.2}(OH)_2(NO_3)_{0.2}(s) + HCONH_2(aq)$ $\rightarrow [Mg_{0.8}Al_{0.2}(OH)_2]^+ [(NO_3)_{0.2}]_{(s)}^-$

Equation 2 The chemical reaction of MgAI LDH after dispersing in aqueous formamide

The digital photograph of colloidal MgAI LDH NS is shown in Figure 62a. Magnesium nitrate hexahydrate (Mg(NO₃)₂ • 6H₂O) and Aluminum nitrate nonahydrate (Al(NO₃)₃ • 9H₂O) were used as starting materials for the synthesis of MgAI LDH NS *via* co-precipitation method. The 23 vol% formamide solution was used as an inhibitor of the layer stacks. The molecules of formamide would attach to the LDH surface, which can allow the LDH to be in the form $[Mg_{0.8}AI_{0.2}(OH)_2]^+$ NS by impeding the individual LDH layers from coming together and stacking as shown in Figure 62b. Finally, LDH is typically determined with the formula $[Mg_{0.8}AI_{0.2}(OH)_2]^+$ [(NO₃)_{0.2}]⁻_(s).

The Tyndall effect for MgAl LDH was referred to the scattering of light towards colloidal-sized particles distribution in the suspension as shown in Figure 62c. This effect was used to confirm the dispersion stability of MgAl LDH nanosheets and particles within the colloidal solution (88, 102, 103). The MgAl LDH particles are suspended in a liquid medium and can be dispersed as colloidal solutions.



Figure 62 The obtained MgAI LDH NS colloidal (a), the formation of single layer nanosheets by direct growth with the incorporation of layer growth inhibitors (b), and Tyndal effect of MgAI LDH NS colloidal (c)

4.1.1.2. The morphological characterization of MgAI LDH NS

To analyze the morphology of MgAI LDH NS in more detail, the SEM technique is used. By preparing the MgAI LDH NS sample was used *via* drop casting technique (104). The drop casting technique for SEM sample preparation involves placing a small drop of a dispersed powder or nanoparticle solution onto SEM sample stub as shown in Figure 63. After dropping the solution, it is allowed to dry at room temperature or under mild heating to evaporate the solvent and leave it behind an even layer of the dispersed material on the substrate. Once dried, the sample may be coated with a thin conductive layer (e.g., gold or carbon) to prevent charging during SEM imaging. This technique is simple and effective for preparing samples for SEM analysis.

The SEM image of MgAI LDH NS characterization was studied by SEM technique at 10kX magnification as shown in Figure 64. The stacked sample revealed the presence of MgAI LDHs in plate-like shape with micron size thickness that is consistent with the MgAI LDH morphology illustrated in a later study by Naik, B. and colleagues (105). Furthermore, the EDS analysis was further used to confirm the elemental components of the MgAI LDH NS. The results of the EDS with color mapping images of oxygen (O), aluminum (Al) and magnesium (Mg) in the sample are displayed as blue, yellow and orange (Figure 65). The EDS analysis can identify the O, Mg and Al within 63.80 wt%, 24.94 wt% and 11.26 wt%, which is consistent with the presence of Mg-O and Al-O in its chemical structure (88, 106). EDS analysis can be used to support SEM images to preliminary confirm the success of MgAI LDH NS *via* co-precipitation method.



Figure 63 Illustration of drop casting technique for SEM sample preparation.



Figure 64 SEM image of MgAI LDH NS at 10kX magnification



Figure 65 EDS spectrum and Elemental color mapping of MgAI LDH NS

4.1.1.3. The chemical structural characterization and phase identification of MgAI LDH NS

The functional groups, chemical bonding characteristics and phase identification were determined to identify the molecular structure of MgAI LDH NS by using ATR-IR, and XRD techniques. The colloid was centrifuged, and the precipitate was used for further characterizations. The samples of MgAI LDH NS were dried under atmospheric conditions. The dried sample was ground together with potassium bromide (KBr) and pressed as a pellet. The ATR-IR spectra is shown in Figure 66 within the region between 4000-550 cm⁻¹. All ATR-IR peaks corresponding to MgAI LDH NS with chemical bonding are summarized in Table 6. The intensive broad band assigned to the stretching vibration of the O-H bond (ν -OH) is present around 3500-3250 cm⁻¹. The band at 1638 cm⁻¹ is attributed to the O-H bending vibration (δ -OH). These two distinct bands are characteristics of the hydroxyl group in water that is generally present in the MgAI LDH NS structure. All the above mentioned peaks correspond to the characteristic MgAI LDH NS peak reported in the literature and show that MgAI LDH NS is completely synthesized (38). The peak at 1357 cm⁻¹ is attributed to the vibration of the stretched nitrate ions in the interlayer. The stretching of M-O and O-M-O groups (M = Mg²⁺, Al^{3+}) are assigned to the bands around $800-600 \text{ cm}^{-1}$.

The XRD pattern of MgAl LDH NS, as shown in Figure 67, was illustrated by collecting data over 2**0** range of $10-70^{\circ}$ within a step size of 0.02° . The peak at 11° , 23° , 35° , 39° , 46° , and 60° belong to the (003), (006), (012), (015), (018), and (110) crystal planes (107, 108), which is consistent with the JCPDS (Joint Committee on Powder Diffraction Standards) database standards number 37-0630 (108).

To confirm the crystal structure, LeBail refinement using JANA2006 software was used. The JANA2006 is an advanced software tool that is used for crystallographic analysis, specializing in the refinement of complex, modulated, incommensurate, and composite structures. The refinement reports provide detailed output summarizing the refinement results, including final atomic positions, bond lengths, angles, and displacement parameters. Figure 67 presents the result by

demonstrating the refinement peak (blue line), the experimental peak (black + symbol), the shift patterns (red line) and the Bragg peak positions (vertical black bar). The LeBail results confirmed that the MgAI LDH exhibits a hexagonal crystal structure. However, LeBail refinement is a method used in X-ray diffraction (XRD) analysis to fit the diffraction pattern and extract crystallographic information without assuming specific atomic positions in the structure. The reliability parameters determine the accuracy and reliability of refined models when evaluating refinement processes, particularly in crystallographic studies. Among these, the Profile Factor (Rp), the Weighted Profile Factor (Rwp), and the Goodness of Fit (GOF) are paramount (109). Thus, the LeBail refinements use statistical indicators like Rp, Rwp, and GOF to assess how well the calculated diffraction pattern matches the experimental data. These parameters help to evaluate the quality of the refinement. In this work, the refinement of MgAI-LDH crystals (CIF number 2102792) provides the fitting parameters within the Rp = 2.47, Rwp = 3.60and GOF = 1.46, which shows well-fitting parameters. The lattice parameters were also determined to be $a = b = 3.045 \pm 0.00024$ Å and $c = 23.337 \pm 0.00242$ Å. As mention the refinement methods and parameters are crucial for analyzing and interpreting XRD data ensuring accurate characterization of crystalline materials.

Furthermore, the basal spacing was further studied. The basal spacing corresponds to the formation of the lamellar layer formed by the divalent/trivalent cations, which is supported by an interlamellar layer containing the hydrated anion to neutralize the charges and to support the stacking of the hydroxide layers (110). This spacing includes both the thickness of the layers and the space between interlamellar layers, which can be filled with water, anions, or other molecules. It is an important structural parameter in materials science particularly in understanding the properties and behavior of layered materials. The basal spacing was calculated in accordance with the Bragg equation, according to the equation 3;

$$d = \frac{n\lambda}{2sin\theta}$$

Equation 3 Bragg equation

, where *d* is the spacing of the crystal layers (path difference), *n* is an integer, λ stands for wavelength of x-ray radiation (1.5418 Å), and θ is the angle of diffraction. In this work, the LDH demonstrate the characteristic peaks of hydrotalcite materials with symmetrical reflections for the planes (d₀₀₃), (d₀₀₆), and (d₁₁₀) and asymmetric reflections for non-basal planes (d₁₁₂), (d₁₁₅), and (d₁₁₈) (107, 110), which is calculate only the planes of (d₀₀₃). The basal spacing (d₀₀₃) of MgAl LDH corresponding to the intercalation of NO₃⁻ anions (111) is shown in Figure 68, which was found to be 0.76 nm. It agrees with the interlayer spacing of 0.75 - 0.76 nm reported in the literature (107, 110). This basal spacing is a key characteristic of MgAl LDH corresponding to the spacing between the positively charged metal hydroxide layers and the intercalated anions and water molecules within the interlayer spaces.

The average crystallite size is also calculated using the Debye Scherrer formula, according to the equation 4:

$$D = \frac{K\lambda}{\beta cos\theta}$$

Equation 4 The Debye Scherrer formula

, where *D* is crystallite size, *K* denotes Scherrer's constant (*K* = 0.94; following to the literature (112)), λ stands for wavelength of x-ray radiation (1.5418 Å), β is a full width at half maximum (FWHM) of a diffraction peak, and θ is the angle of diffraction. From the Debye-Scherrer equation, the calculated D is 89.0 ± 9.6 nm, which is in good agreement with the literature (113).

The energy band gap (E_g) can be calculated following the Tauc's plot. It was originally developed in the early 1970s to investigate energy band gap in semiconductors (114). It is particularly useful for the band gap energy of a material from its absorption spectrum. The band gap energy of MgAl LDH NS calculates by equation 5;
$$\alpha h \nu^{\gamma} = A(h\nu - E_g)$$

Equation 5 Tauc's plot relation

which α is the absorption coefficient, h is Planck's constant, ν is the frequency of the incident photon, γ is the exponent equal to 2, A is a proportionality constant, E_g is the bandgap energy. The energy band gap is a critical property that influences the electronic and optical behavior of materials. Tauc's plot is a widely used technique to estimate the energy band gap of materials, showing by plotting the quantity $\alpha h \nu^{\gamma}$ against the photon energy $h\nu$. The extrapolating the linear portion of the plot to the x-axis the intercept gives the estimated energy band gap of the material. In this case of MgAI LDH NS, the energy band gap is found to be around 5.5 eV as shown in Figure 69. This value corresponds well with other findings, which reported energy gaps in the range of 5.06 to 5.58 eV (115). Therefore, based on all the characterization results the success of MgAI LDH NS synthesis can be confirmed (116).



Figure 66 ATR-IR spectra of MgAI LDH NS

Table 6 ATR -IR spectral data of MgAI LDH NS

Wavenumber (cm ⁻¹)	Characteristic bonds
3500-3250	-OH stretching vibration
1638	-OH bending vibration
1357	$-NO_3^{-}$ stretching vibration
800-600	Metal-oxide stretching vibration (Mg-O and Al-O)



Figure 67 XRD pattern of MgAI LDH NS



Figure 68 schematic representation of MgAI LDH crystal structure and the plate-like



Figure 69 Energy band gap of MgAI LDH NS

4.2. Silk Fibroin (SF) system

4.2.1. SF composite film (charge generating layer) characterization

SF film is a biomaterial derived from silk, which is primarily derived from the silkworm Bombyx mori. In accordance with the SF system, the SF film was firstly chosen to be composited with MgAI LDH NS as charge generating layer for the fabrication of the S-TENG device. For the structural design, an additional layer of SF/lignin is added as intermediate layer, which stands for charge trapping layer for the fabrication of the M-TENG. The results and discussion are reported by beginning with the characterization of SF system, including silk cocoons, silk fibers, SF films, and SF composite film, respectively.

4.2.1.1. The characterization of silk cocoon and degummed silk fiber

Various techniques were used to characterize the silk cocoon and degummed silk fiber. The morphology of silk cocoon and degummed silk fiber were examined by digital imaging and SEM technique. In addition, ATR-IR, Raman and XRD were used for chemical structural characterization and phase identification.

4.2.1.1.1. The morphological characterization of silk cocoon and degummed silk fiber

A silk cocoon is the natural casing spun by silkworms during their transformation from larva to pupa. It is primarily made of fibroin, a structural protein, but also contains sericin, a glue-like protein that holds the silk fibers together. In addition, the degummed silk fiber refers to the silk fiber after the sericin has been removed through a process called degumming process. This process involves boiling the silk cocoons in an alkaline or soapy solution (117), which removes the sericin and leaves behind the pure silk protein fibroin. After the degumming process, the fibers were immediately washed with DI water to a neutral pH and dried. According to the digital photograph of silk cocoon (raw silk) and degummed silk fiber before and after degumming process are shown in Figure 70a and b.

The morphology of silk cocoon and degummed silk fiber was studied by SEM technique at 1000X magnification. The SEM images are shown in Figure 70c and d. According to Figure70c, the surface morphology of silk cocoon shows the fibers coated with a rough, uneven layer of sericin, which is the natural gum for binding the silk filaments together. The fibers appear clustered with a less-defined structure due to the presence of this sticky substance. This coating gives the cocoon its protective qualities but also hides the smoother fibroin core, which becomes visible only after the degumming process. It was also reported by Samie M. and co-workers (118). The sericin was completely eliminated during the degumming process. The silk fibers are revealed as smooth and uniform fibers after the removal of sericin as shown by SEM image in Figure 70d, in which the fibroin fibers are entirely separated from each other and show the smooth fiber with a smooth surface. As shown in Table 7, the diameter of the silk cocoon and silk fibers was approximately 25.57 ± 1.3 and 9.02 ± 0.6 µm, respectively. The degumming ratio (D,), the change in weights of the samples before and after degumming, was used to evaluate the degumming ratio or weight loss, that can be calculated according to equation 6:

$$D_r = \frac{W_0 - W_1}{W_0} \times 100$$

Equation 6 The degumming ratio or weight loss measurement

, where W_0 refers to the weight of the dried silk before the degumming process and W_1 refers to the weight of the dried silk after the degumming process (119). In this work, the D_r was found to be 29.9%, which is agrees well with the degumming process by using sodium bicarbonate (Na₂CO₃) solution (120). The degummed silk fiber was used to prepare the SF solution using Ajisawa's method. The SF film was subsequently fabricated by casting.



Figure 70 Digital images of raw silk (a) and degummed silk fiber (b) and the SEM images of raw silk (c) and degummed silk fiber (d) at 1000X magnification

	Raw silk at 1000X	Degummed silk fiber 1000X		
Fiber diameter	25 57 ± 1 2	0.02 ± 0.6		
(Mean ± SD, µm)	20.07 I 1.0	9.02 ± 0.0		

Table 7 The fiber size of raw silk and degummed silk fiber

4.2.1.1.2. The chemical structural characterization and phase identification of silk cocoon and degummed silk fiber

Additionally, the morphological study, the functional groups, chemical bonding characteristics and phase identification were determined to identify the molecular structure of silk cocoon and degummed silk fiber by ATR-IR, Raman, and XRD techniques. The ATR-IR spectra are shown in Figure 71 in the region between 4000-550 cm⁻¹. All ATR-IR peaks corresponding to silk cocoon and degummed silk fiber molecules with chemical bonding are summarized in Table 8. The characteristic peaks of the silk cocoon can be observed by the broadband at 3286 cm⁻¹, which was assigned to the stretching vibration of the O-H (ν O-H) and N-H (ν N-H) groups overlapping. There are three absorption peaks around 1620, 1518, and 1234 cm⁻¹ characteristic of C=O stretching vibration (ν C=O), C-N stretching vibration (ν C-N), and C-N bending vibration (δ C-N), which indicated the Amide I, Amide II and Amide III bonding, respectively. However, the absorption peak at 1234 cm⁻¹ was assigned to the β -sheet. In particular, the amide bands associated with the β -sheet conformation did not change after degumming. The IR results confirmed the chemical functional group of raw silk and degummed silk fiber (121, 122).

This is additionally confirmed by Raman spectroscopy as shown in Figure 72, where similar spectra were determined for both samples. According to the Raman spectra are shown in the region between 3500-500 cm⁻¹. The broaden peak at 3450-3250 cm⁻¹ is combination of O-H (vO-H) and N-H (vN-H) groups. The characteristic peaks of the fibroin structure are identified at 3062, 2935, and 2876 cm⁻¹, corresponding to C-N-H bending (δ C-N-H), CH₂ asymmetric stretching (ν_{ac} CH₂) and CH₂ asymmetric stretching (vCH_2), respectively from amino acid skeleton (123). The bands relating to the β -sheets of amide I and amine III confirmed the crystallized regions. Amide I of the β sheet of the C=O stretching vibration (vC=O) is assigned to the peak at 1620 cm⁻¹ (124). The two peaks around at 1443 and 1393 cm⁻¹ has been investigated, conforming to CH₂ scissoring (scis- δ CH₂), which is one vibration mode of bending, and CH₂ (δ CH₂) bending (125). The band at 1256 cm⁻¹ in amide III also indicates a β -sheet structure. The short side chain of the repetitive Gly-Ala-Gly-Ala-Gly-Ser amino acid sequence is well known to dominate the crystalline region. The arrangement in the amorphous region contains many amino acid residues, such as lysine, tyrosine, and arginine, among others, which are composed of nonrepetitive amino acid sequences (126). The list of Raman shifts matched with the chemical bonds was shown in table 9 and the Raman

results confirmed the chemical functional group of raw silk and degummed silk. The Raman technique can also be used to support ATR-IR results in this work for the confirmation of the chemical structure of silk cocoon and degummed silk fiber. Which can be from the characterization results that the main structure was not change after degumming process.

The XRD pattern of silk cocoon and degummed silk fiber was analyzed by using X-ray diffraction (XRD). The data was collected over angular range of two theta (2θ) about 10-80° with a step size of 0.02° as shown in Figure 73. The pattern exhibits distinct peaks at 2 θ values of approximately 19° and 28°, which indicates the crystalline β -sheet structure within the silk fibroin. In addition, a broad peak was observed due to the existence of amorphous regions within the silk fibroin film. The silk fibroin film is composed of both crystalline and amorphous phases due to the combination of sharp and broad peaks. Which agreed with the results reported (127, 128).



Figure 71 ATR-IR spectra of raw silk, and degummed silk fiber



Figure 72 Raman spectra of raw silk, and degummed silk fiber

Table 8 ATR-IR spectral data of raw silk and degummed silk fiber

Wavenumber (cm ⁻¹)	Characteristic bonds
3286	-OH overlap -NH ₂ stretching vibration
1620	C=O stretching vibration (Amide I)
1518	C-N stretching vibration (Amide II)
1234	C-N bending vibration (Amide III)

Raman shift (cm ⁻¹)	Characteristic bonds	
3450-3250	-OH overlap -NH ₂ stretching vibration	
3062	C-N-H bending vibration	
2935	$-CH_3$ asymmetric stretching vibration	
2876	-CH ₂ asymmetric stretching vibration	
1620	C=O stretching vibration (Amide I)	
1443	-CH ₂ scissoring bending vibration	
1393	-CH ₃ bending vibration	
1256	β -sheet structure (Amide III)	

Table 9 Raman spectral data of raw silk and degummed silk fiber



Figure 73 XRD pattern of raw silk, and degummed silk fiber

4.2.1.2. The characterization of silk fibroin (SF) film

Various techniques were used to characterize the SF film. The morphology of SF film was examined by digital imaging and SEM techniques. In addition, ATR-IR, Raman, and XRD were used for chemical structural characterization and phase identification.

4.2.1.2.1. The morphological characterization of SF film

The obtained SF solution's image is shown in Figure 74a. After obtaining SF solution, it was cast into the PS mold and dried overnight in a hot air oven at 45°C to get the SF film as shown in Figure 74b, which was transparent. When mechanical force has been applied by folding and rolling. The SF film was cracked as shown in Figure 74c, which is not flexible. For this reason, glycerin and polyethylene glycol (PEG-400) were added to improve the flexibility as mentioned experimentally in Chapter 3.1.3. The digital photograph of the SF film as shown in Figure 75 demonstrates the obtained film within a square size (3 x 3 cm²) and a thickness of 210 \pm 0.08 µm. The physical properties of the SF film were observed in Figure 75a-d, which was transparent and flexible. During applying mechanical force by folding and rolling, as shown in Figure 75b and c, the SF film was not destroyed.

The surface morphology of SF film was examined by using the SEM technique at 40kx magnification, which typically shows a high detail of the morphological surface according to Figure 76. The SEM image result revealed intricate details of its microstructure a smooth and uniform surface texture, showcasing a smooth and homogeneous surface that is characteristic of well-prepared silk fibroin materials. The morphology of the SF film is also reported in the literature (129).



Figure 74 SF solution after dialysis process (a), SF film without glycerin (b and c)



Figure 75 Digital photo of SF film after adding glycerin and PEG-400 (a) flexibility of SF

94



Figure 76 SEM image of SF film at 40kX magnification

4.2.1.2.2. The chemical structural characterization and phase identification of SF film

The functional groups, chemical bonding characteristics and phase identification were determined to identify the molecular structure of SF film by using ATR-IR, Raman, and XRD techniques. The ATR-IR spectra is shown in Figure 77 within the region between 4000-550 cm⁻¹. All ATR-IR peaks corresponding to SF molecules with chemical bonding are summarized in Table 10. The characteristic peaks of the SF film can be observed by the broadband at 3286 cm⁻¹, which was assigned to the stretching vibration of the O-H (ν O-H) and N-H (ν N-H) groups overlapping. Three absorption peaks at around 1620, 1518, and 1234 cm⁻¹ demonstrate the C=O stretching vibration (ν C=O), C-N stretching vibration (ν C-N), and C-N bending vibration (δ C-N), which indicated the Amide I, Amide II and Amide III bonding, respectively. However, the absorption peak at 1234 cm⁻¹ was assigned to the β -sheet. In particular, the amide bands associated with the β -sheet conformation did not change after casting process. The IR results confirmed the chemical functional group of SF molecule (121, 122).

To confirm the SF film, the Raman technique was used, where similar Raman spectra were obtained for both samples. The Raman spectra is shown in Figure 78 within the region between 3500-500 cm⁻¹. The broaden peak at 3450-3250 cm⁻¹ is the combination of O-H (vO-H) and N-H (vN-H) groups. The characteristic peaks of the fibroin structure are identified at 3062, 2935, and 2876 cm⁻¹, corresponding to C-N-H bending (δ C-N-H), CH₃ asymmetric stretching (v_{as} CH₃) and CH₂ asymmetric stretching (νCH_2) , respectively. Those chemical bonds come from amino acid skeleton (123). The bands relating to the β -sheets of amide I and amine III can confirm the crystallized regions. Amide I (β -sheet) of the C=O stretching vibration (ν C=O) is attributed to the peak at 1620 cm⁻¹ (124). The two peaks around at 1443 and 1393 cm⁻¹ has been investigated, conforming to CH₂ scissoring (scis- δ CH₂), which is one vibration mode of bending, and CH₃ (δ CH₃) bending (125). The band at 1256 cm⁻¹ in amide III also indicates a β-sheet structure. The short side chain of the repetitive Gly-Ala-Gly-Ala-Gly-Ser amino acid sequence is well known to dominate the crystalline region. The arrangement in the amorphous region contains many amino acid residues, such as lysine, tyrosine, and arginine, among others, which are composed of nonrepetitive amino acid sequences (126). The list of Raman shifts matched with the chemical bonds is tabulated in table 11. The Raman technique can also be used to support the ATR-IR results for the confirmation of the chemical structure of SF molecule. The main structure did not change after the casting process as can be seen from the characterization results.

The XRD pattern of SF film was analyzed by using XRD. The data was collected over angular range of two theta (2 θ) about 10-50° with a step size of 0.02° as shown in Figure 79. The XRD pattern exhibits distinct peaks at 2 θ values of approximately 12° and 20°, which indicates the crystalline β -sheet structure in the silk fibroin. In addition, a broad peak was observed due to the existence of amorphous regions. Therefore, the SF film is composed of both crystalline and amorphous phases due to the combination of sharp and broad peaks, which is agree well with the results reported above (127, 128).



Figure 78 Raman spectra of SF film

Table 10 ATR-IR spectral data of SF film

Wavenumber (cm ⁻¹)	Characteristic bonds
3286	-OH overlap -NH ₂ stretching vibration
1620	C=O stretching vibration (Amide I)
1518	C-N stretching vibration (Amide II)
1234	C-N bending vibration (Amide III)

Table 11 Raman spectral data of SF film

Raman shift (cm ⁻¹)	Characteristic bonds	—
3450-3250	-OH overlap -NH ₂ stretching vibration	
3062	C-N-H bending vibration	
2935	-CH ₃ asymmetric stretching vibration	
2876	-CH ₂ asymmetric stretching vibration	
1620	C=O stretching vibration (Amide I)	
1443	-CH ₂ scissoring bending vibration	
1393	-CH ₃ bending vibration	
1256	β -sheet structure (Amide III)	



4.2.1.3. The characterization of SF/MgAI LDH NS composite films

To characterize the SF/MgAI LDH NS composite film with variety of techniques were employed. The film's morphology was thoroughly analyzed using digital imaging, SEM, and EDS, which provided detailed insights into its surface structure and composition. In addition to morphological studies, the chemical structure and phase identification of the composite were investigated using ATR-IR, Raman spectroscopy, XRD. These techniques collectively allowed for a comprehensive evaluation of the physical and chemical properties of the SF/MgAI LDH NS composite film, enhancing our understanding of its structural characteristics.

4.2.1.3.1. The morphological characterization of SF/MgAl LDH NS composite film

Briefly, the mixing of the SF solution with glycerin, PEG-400, and MgAl LDH NS colloidal at 0.5, 1, 1.5, 3, 6 and 12%(v/v) was stirring continuously for 10 minutes. Then pour the mixed solution into the PS mold and dry in the hot air oven at

 45° C overnight. The digital photograph of SF/MgAl LDH NS composite film is shown in the square size 3 x 3 cm². The thickness of composite films was raised when adding more MgAl LDH NS between 0.5, 1, 1.5, 3, 6 and 12%(v/v) for 283 ± 0.02, 285 ± 0.05, 286 ± 0.08, 286 ± 0.03, 288 ± 0.04, and 289 ± 0.07 µm, respectively. All the thickness details are summarized in Table 12. The obtained SF/MgAl LDH films with various amounts of MgAl LDH NS according to 0.5, 1, 1.5, 3, 6, and 12% (v/v) are shown in Figure 80. After adding the MgAl LDH NS, all the SF/MgAl LDH NS composite films were colorless and still transparent, as can be seen clearly through the background. Upon applying mechanical force to the SF/MgAl LDH NS composite films by folding and rolling, all the films can be deformed and returned the shape to the same initial state.

To make the discussion more scientific, the physical property of SF/MgAI LDH NS composite film was analyzed using UV-vis spectrophotometer. That was an essential tool for understanding the interaction of light with materials. Thus, the optical transmittance of SF film and three various amounts of the MgAI LDH NS at 1, 3, and 12%(v/v) in the range of 350-800 nm is shown in Figure 81. It was found that all composite films demonstrated a decrease in light transmission in the visible part of the spectrum as the amount of MgAI LDH NS increased. Incidentally, all composites exhibited the same physical properties. For the pristine SF film and three different contents of MgAI LDH NS loading at 1, 3, and 12%(v/v), respectively. Nevertheless, all the composite films achieved more than 70% transmission. As a result, it was confirmed that the successful fabrication of the SF/MgAI LDH NS composite film.

The surface morphology of the SF film and the SF/MgAI LDH NS composite film was compared by using the SEM technique at the same magnification of approximately 40kX. The results indicate that the SF film exhibited a smooth and uniform surface, demonstrating effective film formation and consistent material processing as shown in Figure 82. However, after adding more amounts of MgAI LDH NS, all the SF/MgAI LDH NS composite films show an increase in roughness and the presence of the filler phase within the matrix as can be seen in Figure 82b-d. This confirms the successful fabrication of the SF/MgAI LDH NS composite film. In addition, the EDS

analysis was further used to confirm the elemental components of 1%(v/v) MgAI LDH NS loading. The results of the element mapping image with detection graph of oxygen (O), aluminum (AI) and magnesium (Mg) in the sample with different colors of blue, yellow and orange is reported within 100 wt%, 0.00 wt% and 0.00 wt% (Figure 83). The Mg and AI were not detected at 1% of MgAI LDH NS loading. The percentage of O, Mg and AI elements was begun to be detectable at 3% of MgAI LDH NS. The Mg and AI percent was further increased as the loading was increased to 12% according to Figure 84 and 85 confirming the existence of MgAI LDH phase on SF matrix.

To achieve high-performance compositing properties, appropriate content with high dispersibility was required. Therefore, the 3D virtualization of morphology using SR-XTM was investigated. The SR-XTM technique was used to investigate the dispersion of the MgAI LDH NS phase within the SF/MgAI LDH NS composite film, which gives a result in terms of 3D virtualization images. The virtualization image of the SF/MgAI LDH NS composite film is shown in Figure 86a-c. The purple-colored phase is represented the MgAI LDH NS, while the gray-colored phase is identified as the SF matrix. However, a lower amount of 1% of MgAI LDH NS loading was found to contain less MgAI LDH NS in the SF matrix. Furthermore, a greater amount of MgAI LDH NS was incorporated into the SF matrix with a homogeneous and well dispersed morphology at higher ratios of 3% and 12% of MgAI LDH NS loading. The result clearly indicated that the MgAI LDH NS can be dispersed with incorporation into the SF matrix.



Figure 80 Digital photographs of SF/MgAI LDH before & after folding and rolling

SF/MgAI	Digital	Color &	Surface	Flexibility	Thickness
LDH %(v/v)	photographs	Transparent	morphology	property	(µm)
0.5		Colorless & Transparent	Rough	Flexible	283 ± 0.02
1		Colorless & Transparent	Rough	Flexible	285 ± 0.05
1.5		Colorless & Transparent	Rough	Flexible	286 ± 0.08
3		Colorless & Transparent	Rough	Flexible	286 ± 0.03
6		Colorless & Transparent	Rough	Flexible	288 ± 0.04
12		Colorless & Transparent	Rough	Flexible	289 ± 0.07

Table 12 Summarization of physical property of SF composite films with various amounts of MgAI LDH NS



Figure 81 The transmittance of SF/MgAI LDH NS at 1% (a), 3% (b), and 12%(v/v) (c)



Figure 82 SEM image of SF film (a), SF/MgAI LDH NS 1% (b), SF/MgAI LDH NS 3% (c), and SF/MgAI LDH NS 12% (d) at 40kX magnification



Figure 83 EDS spectrum and Elemental mapping of SF/MgAI LDH NS 1%(v/v)



Figure 84 EDS spectrum and Elemental mapping of SF/MgAI LDH NS 3%(v/v)



Figure 85 EDS spectrum and Elemental mapping of SF/MgAI LDH NS 12%(v/v)



Figure 86 SR-XTM 3D virtualization of SF/MgAl LDH NS at 1%(v/v) (a), SF/MgAl LDH NS 3%(v/v) (b), and SF/MgAl LDH NS 12%(v/v) (c)

4.2.1.3.2. The chemical structural characterization and phase identification of SF/MgAI LDH NS composite film

Besides the morphological study, the functional groups and chemical bonding characteristics were analyzed by ATR-IR in the range of wavenumber 4000-550 cm⁻¹. The results are shown in Figure 87. It was found that all the peaks were similar to those obtained by the SF film, as mentioned above. Consequently, the broad band at 3286 cm⁻¹ is explained by the combination of stretching vibration of O-H (*v*O-H) and N-H (*v*N-H), which can be identified as the characteristic peaks of the silk structure. There are three absorption peaks around 1620 cm⁻¹, 1518 cm⁻¹ and 1234 cm⁻¹ that are characteristic of C=O stretching vibration (*v*C=O; amide I), C-N stretching vibration (*v*C-N; amide II) and C-N bending vibration (*b*C-N; amide III), respectively. The absorption peak at 1234 cm⁻¹ was attributed to the β -sheet configuration. There was no change in the amide bands corresponding to the β -sheet configuration after casting process. The IR results confirmed the chemical functional group of SF film. The specific absorption peaks for Al-O and Mg-O groups could explain the bands observed around 600–800 cm⁻¹ (116) could not be detected due to the low concentration of the incorporated MgAl LDH NS.

The XRD pattern of SF/MgAl LDH NS composite film was analyzed by using X-ray diffraction (XRD). The data was collected over angular range of two theta (2θ) about 10-40° with a step size of 0.02 o as shown in Figure 88. The pattern only exhibited the distinct peaks at 2 θ values of approximately 12° and 20°, which indicated the Silk I structure (random coil content) and Silk II crystal structure (β -sheet content). The broadening of these peaks suggests that SF becomes more amorphous after the addition of MgAl LDH NS fillers (130, 131). Probably the MgAl LDH NS is embedded between the SF polymer chains, disrupting the ordering. In addition to the relatively small amount of incorporated LDH filler, the lack of such reflections suggests that they may be highly dispersed.



Figure 87 ATR-IR spectra of SF film and SF/MgAI LDH NS composite films



Figure 88 XRD pattern of SF film and SF/MgAI LDH NS composite films

4.2.2. The working mechanism and electrical output performance of SF/MgAl LDH NS composite films for S-TENG device

4.2.2.1. The working mechanism of SF/MgAl LDH NS composite films composite film as charge generating layer for S-TENG device

The working diagram of Bio-based composite film (SF-Based and BC-Based condition) as the S-TENG, which was operated in vertical contact separation (VCS) mode as shown in Figure 89. When an external force was continuously applied to the FS-TENG device, the triboelectrification and electrostatic induction were obtained (60). In the initial stage (I), when these two different materials, Bio-Based composite films and PTFE films were contacted, the difference of electronegativity of their material would be led the charges exchange. Strong electron-donating tendency from the amine group (-NH₂) of SF (13) and the hydroxyl group (-OH) of BC (22) were induced the positive charges occurrence on the surface of Bio-Based composite film. Meanwhile, the PTFE film is exposed to the strong electron withdrawing behavior of the fluorine atom (-F). This was generated a negative charge on the PTFE surface. As the materials had continuously contacted each other at this stage, the device situation remained in a neutral state. It was not possible to generate an electric field. After separating the two films following to state (II), the charge disequilibrium was induced the occurrence of opposite charges on each side of the electrodes, this was generated a small electric field causing electrons to flow to the load. Until the charge flow reaches equilibrium in state (III), a positive electrical output is provided. As soon as the two films were contacted with each other again (state IV), the electron flowed back in the opposite path and ultimately acquired the entire loop of an alternating electrical signal waveform (AC). However, the FS-TENG device in this work was classified into the dielectric-to-dielectric type of TENG (132), the output efficiency mainly relied on the electrical potential difference (V), the charge density (Q) and the distance (x) between the layers, which has been described as the V-Q-x relationship. The V-Q-x relationship, which V or V_{gap} is the voltage between two conductive electrodes, Q is the amount of charge transferred, and x is the separation distance between two tribomaterials (133). Thus, The V-Q-x relationship is followed by Equation 7.

$$V_{gap} = -\frac{Q}{S\varepsilon_0} \left(\frac{d_{\text{PTFE}}}{\varepsilon_{\text{PTFE}}} + \frac{d_{\text{Bio-Based composite film}}}{\varepsilon_{\text{Bio-Based composite film}}} + x(t) \right) + \frac{\sigma x(t)}{\varepsilon_0}$$

Equation 7 The V-Q-x relationship of dielectric-to-dielectric type of TENG in VCS mode.

where *Q*, *S*, *d* and *x* are the induced charges, the contact area of the electrode, the thickness of the friction layer and the distance between the two friction layers. The σ is triboelectric charge density. The ε_0 , ε_{PTFE} and $\varepsilon_{Bio-Based composite film}$ referred to the relative permittivity of vacuum, PTFE film and Bio-Based composite films respectively. The electrical output in terms of open circuit voltage (V_{oc}) and short circuit current (I_{sc}) could be determined from the Equations 8 and 9 (134, 135).

$$V_{OC} = \frac{\sigma x(t)}{\varepsilon_0}$$

Equation 8 The open circuit (V_{oc}) condition

$$I_{SC} = \frac{S\sigma d_0 v(t)}{(d_0 + x(t))^2}$$

Equation 9 The short circuit (I_{sc}) condition

where v(t) determined to the relative velocity of the friction materials, while d_0 described the effective thickness in terms of $\left(\frac{d_{PTFE}}{\epsilon_{PTFE}} + \frac{d_{Bio-Based composite film}}{\epsilon_{Bio-Based composite film}}\right)$. The V_{oc} and I_{sc} of the Bio-Based FM-TENG with the different content of MgAl LDH NS at 0.5, 1, 1.5, 3, 6 and 12%(v/v) were evaluated.



Figure 89 The working diagram of Bio-Based composite as the FS-TENG based on vertical contact separation (VCS) mode

4.2.2.1.1. The electrical output performance of SF/MgAl LDH NS composite films composite film as charge generating layer for S-TENG device

Briefly, the SF/MgAI LDH NS/S-TENG was fabricated in the form of a VCS mode. The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribo-material pair movement during the VCS process. The SF/MgAI LDH NS composite films were cut into 3 x 3 cm², and the AI tape was used as an electrode with Cu wire connections as shown in Figure 90. The electrical output of the SF/MgAI LDH NS composite films for S-TENG device was measured and analyzed using an oscilloscope and digital multimeter. Thus, the TENG was periodically mechanically tapped using a linear motor to simulating

mechanical stimulation. The $V_{\rm oc}$ and $I_{\rm sc}$ were read and recorded at different frequencies and amplitudes. By measuring the voltage against different load resistances, the power density was calculated. The electrical output of the SF/MgAI LDH NS composite film as FS-TENG device was tested using an oscilloscope and a digital multimeter to demonstrate the $V_{\rm oc}$ and $I_{\rm sc}$ under VSC mode. As shown in Figure 91 and 92. The SF film demonstrated V_{oc} and I_{sc} of 63 V and 481 μ A. By adding the MgAl LDH NS, which resulted in the improvement of electrical output. As the content of MgAI LDH NS was increased at 0.5, 1, 1.5, and 3%(v/v), the V_{oc} and I_{sc} signals also increased significantly. That provided about 68, 71, 74, and 80 V, and 500, 541, 556, and 600 µA, respectively. The result obtained the highest $V_{\rm oc}$ and $I_{\rm sc}$ at 3%(v/v) of MgAI LDH NS loading. Nevertheless, by increasing the MgAI LDH NS content to 6 and 12%(v/v), both of $V_{\rm oc}$ and I_{sc} signals were decreased to 77 V, 520 μ A and 69 V, 496 μ A respectively. Due to the agglomerated behavior of the filler particles were reduced the effective surface area, thereby also reduced the interfacial polarization (136). Furthermore, the agglomerated particles generate internal voids and defects which reduce the dielectric properties of the nanosheet (NS). Consequently, the dipole orientations disordered, producing weak inductive charges and electrical performance (86, 137). The maximum output power P_{max} of SF film and SF/MgAI LDH NS composite film was tested under the resistance range 100 Ω – 100 M Ω . Power is determined by the output power relationship is following the equation 10.

$$V = \frac{I}{R}$$

Equation 10 The Ohm's law

, where V is the voltage across the electrical component (V), I is the current flowing through the component (A), R is the resistance of the component (Ω). Thus, the $V_{\rm oc}$ was increased as the external load resistance increasing from 100 Ω to 100 M Ω , and the $I_{\rm sc}$ was decreased as the external load resistance decreasing to 100

M Ω , as shown in Figure 93 and 94. The P_{max} of the SF film was around 100 μ W at 5 M Ω external load resistance, corresponding to a power density of 11.1 μ W/cm². The higher P_{max} of 165 μ W with a power density of 18.3 μ W/cm² was achieved by adding 3%(v/v) of MgAI LDH NS. The power density increased 1.6 times.



Figure 90 Schematic diagram of SF/MgAI LDH NS as the S-TENG based on VCS mode



Figure 91 The $V_{\rm OC}$ of SF film and SF/MgAl LDH NS composite films



Figure 92 The $I_{\rm SC}$ of SF film and SF/MgAI LDH NS composite films



Figure 93 The P_{max} of SF film



Figure 94 The P_{max} of SF/MgAI LDH NS 3%(v/v) composite film

4.2.2.2. The important role of MgAI LDH NS in S-TENG device

SF contains abundant -NH₂ groups with the network formed *via* peptide bond (C=(O)NH-) /or Amide bond as shown in Figure 95a. The peptide backbone of silk fibroin is composed primarily of the amino acids glycine (Gly), serine (Ser), and alanine (Ala). These three amino acids form repeating sequences that can fold into highly ordered structures like β -sheets. A peptide bond is a covalent bond that forms between two amino acids. It occurs when the carboxyl group (-C=(O)OH-) of one amino acid reacts with the amino group (-NH₂) of another. Meanwhile, MgAI LDH NS in which the dominant anionic group is hydroxide (OH⁻) anions are present at the surface as shown in Figure 95b. Furthermore, the silk fibroin is composed of crystalline areas that offer strength and rigidity, formed by the alignment of β -sheets in parallel patterns. The amorphous random coil areas that provide flexibility and elasticity are distributed throughout the crystalline β -sheet structure (138). Silk has a unique combination of the toughness and stretchability due to its ordered and disordered areas as shown in Figure 95c. By adding the MgAI LDH NS into SF solution, the H-bond between O and H atoms of MgAI LDH NS and -NH₂ of SF could be responsible for this mechanical integrity. This result was supported the XRD pattern of SF and SF/MgAI LDH composite films. The crystalline regions of silk fibroin are formed primarily by tightly packed β -sheets, which contribute to the material's strength and durability. These β -sheets are held together by intermolecular forces, including hydrogen bonds between the peptide chains, van der Waals forces, and hydrophobic interactions. In the crystalline structure, hydrogen bonds play a key role in stabilizing the β -sheet conformation. These bonds form between the carbonyl oxygen and the amide hydrogen in the peptide backbone, ensuring the alignment and stability of the β -sheets. When the polar molecules are introduced, they can interact with the silk fibroin. The polar molecules can form their own hydrogen bonds with the carbonyl and amide groups in the fibroin, which disrupting the existing hydrogen bonds that stabilize the β -sheets. This can cause the orderly structure of the crystalline regions to break down, leading to a loss of crystallinity. In essence, the polar molecule competes with the hydrogen bonds that maintain the β -sheet structure, making the fibroin more amorphous. The amorphous transformation of SF with the addition of LDH fillers is indicated by the broadening of two peaks. This ordering is most likely destroyed by the incorporation of the MgAI LDH NS between the SF polymer chains. Apart from the relatively little amount of LDH filler provided, the lack of these reflections implies that they could be widely distributed (130, 139). In summary, hydrogen bond disruption by external molecules (such as water) leads to the destabilization of the β sheet regions in silk fibroin, breaking down the crystalline structure as shown in Figure 95d.

However, hydrogen bonds are essential to molecular interactions at the material-material interface, especially when polymers or organic molecules are involved. These bonds may have an impact on the generation and retention of surface charges during contact electrification, often known as the triboelectric effect. The formation of hydrogen bonds has the potential to influence the electronic environment of the constituent atoms, thereby impacting the material's capacity to acquire or shed

electrons when in contact with another surface. Moreover, it was observed that materials with higher hydrogen-bonding potential not only generated more surface charge but also retained it for a longer duration compared to materials with fewer hydrogen bonds. This suggests that hydrogen bonds enhance charge retention by stabilizing the charges at the interface, potentially by reducing the recombination of free electrons with opposite charges from the environment (140). Hydrogen bonds not only affect charge retention but also influence the electron transfer mechanism. The formation of hydrogen bonds at the interface between materials can lead to a localized polarization effect. This effect changes the electronic environment of constituent atoms, reducing the energy barrier for electron transfer during contact electrification (141). In order to improve the output performance of TENGs, this could lead in an increase in surface charge density (142).

Additionally, The addition of the dielectric MgAI LDH NS leads to additional permanent dipole moments, which can be explained by Maxwell-Wagner-Sillars interfacial polarization (MWS-IP) (143), where high charge collection occurred at the interface. The incorporation of MgAI LDH nanosheets in the triboelectric system significantly enhances the electrical output due to the following mechanisms: MgAI LDH nanosheets possess intrinsic dipole moments due to the structure of the material, which consists of positively charged metal hydroxide layers (Mg²⁺ and Al³⁺) balanced by negatively charged interlayer anions. Triboelectric contact between materials creates an electric field at the interface. The dipoles in the MgAI LDH NS orient themselves along this field, increasing the degree of polarization as shown in Figure 96. The electric field formed between the SF/MgAI LDH NS film and the electrode is further enhanced by this dipole alignment, which boosts the separation of charges between the triboelectric materials. The MgAI LDH NS align their dipoles along the field, the polarization between the surfaces of SF/MgAI LDH NS film and the electrode increases. This effect further aids the separation of positive and negative charges across the interface. In simple terms, the combined effect of MWS-IP and the dipole moment alignment leads to a substantial improvement in the electrical output of the TENG.



Figure 95 (a) The peptide backbone of silk fibroin is composed of Gly, Ser, and Ala, (b) The MgAI LDH NS structure, (c) The formation of SF film, and (d) The formation of SF/MgAI LDH film


Figure 96 The schematic diagram of polarization occurrence in SF/MgAI LDH NS

4.2.3. The multilayer structural designed of SF composite film

Before the fabrication of the SF composite film as M-TENG device, the optimum condition for the acquisition of the highest output power of SF/MgAI LDH NS composite film as charge generating layer was obtained. As mentioned above, SF/MgAI LDH NS was achieved the highest V_{oc} and I_{sc} signal 80 V and 600 µA, which was confirmed by adding MgAI LDH NS content of 3%(v/v). In addition, the P_{max} was also determined to be 165 µW with a power density of 18.3 µW/cm². For this reason, it could be concluded that the 3 % (v/v) MgAI LDH NS in SF matrix were used as the charge generating layer. However, the structural design by inserting layer of lignin is added to the intermediate layer as a charge trapping layer. In addition, there are not only discusses the experimental results, but also discusses the scientific understanding the significant role of aromatic lignin structure in the charge trapping layer.

4.2.3.1. The characterization of Lignin

Various techniques were used to characterize lignin. The morphology of lignin was examined by digital imaging. In addition, ATR-IR and XRD were used for chemical structural characterization and phase identification, respectively.

4.2.3.1.1. The morphological characterization of Lignin

Lignin, which is derived from the alkaline pulping process. It is a versatile and abundant natural polymer with a wide range of potential applications (98, 144). The digital photograph of lignin powder as shown in Figure 97. The lignin powder was observed in the dark brown color as clearly shown in the inset image. This result was supported with the literature (145).



Figure 97 Digital photograph of lignin powder

4.2.3.1.2. The chemical structural characterization and phase identification of Lignin

Additionally, the morphological study, the functional groups, chemical bonding characteristics and phase identification were determined to identify the molecular structure of lignin powder by ATR-IR, and XRD techniques. The ATR-IR spectra are shown in the region between 4000-550 cm⁻¹ as shown in Figure 98. The intensive broadband assigned to the stretching vibration of the O-H bonds was found around 3500-3250 cm⁻¹. These bands are representative of the hydroxyl group in phenol. The C=C stretching vibration (ν C=C) observed at 1594 cm⁻¹ attributed to the skeletal vibration of the aromatic ring (Ar-). The characteristic peaks at 1418 cm⁻¹, 1116 cm⁻¹ and 1046 cm⁻¹ attributed to the asymmetric stretching vibration of -CH₃ (ν_{as} -CH₃), the stretching vibration of the asymmetric bridge of C-O-C (v_{as} C-O-C) and the stretching vibration of C-O (vC-O), respectively. All of the identified of IR peaks are in good correlation with the literature (146), In accordance with the substructure, the bands in the spectral region of 855 cm⁻¹, 825 cm⁻¹ and 810 cm⁻¹ were identified as the typical G band (δ_{op} Ar-G), S band (δ_{op} Ar-S) and G band (δ_{op} Ar-G). The list of absorption peaks for lignin was shown in the table 13 and the IR results was confirmed the chemical functional group of lignin (147).

The XRD pattern of lignin powder was analyzed by X-ray diffraction (XRD). The data was collected over angular range of two theta (2 θ) about 10-80° with a step size of 0.02° as shown in Figure 99. To identify the diffraction plane associated with the lignin structure, which can be identified by 2 θ of 31.8°, 34.2°, 37.9° and 46.3° (148-150). That correlates with the crystal planes (100), (002), (101) and (102) of crystalline lignin. Furthermore, the XRD results can be confirmed the lignin that used in this work.



Figure 98 ATR-IR spectra of lignin

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Table 13 ATR-FT-IR spectral data of lignin

Wavenumber (cm ⁻¹)	Characteristic bonds
3500-3250	-OH stretching vibration in phenol
1594	C=C stretching vibration of aromatic ring
1418	-CH ₃ asymmetric stretching vibration
1116	C-O-C asymmetric stretching vibration
1046	C-O stretching vibration
855, 810	substructure G band in lignin
825	substructure S band in lignin



4.2.3.2. The characterization of SF/Lignin composite film as charge trapping layer

The various techniques were used to characterize the SF/Lignin composite film. The morphology of SF/Lignin composite film was examined by digital imaging. In addition, ATR-IR, and XRD were used for chemical structural characterization and phase identification.

4.2.3.2.1. The morphological characterization of SF/Lignin composite

film

As mentioned in Chapter 3.4.3.3. Briefly, the mixing of the SF solution with glycerin, PEG-400, and lignin powder at 0.25, 0.50, 1, and 1.5%(w/v), which was stirring continuously for 10 minutes. Then pour the mixed solution into a PS mold and dried in the hot air oven at 45°C overnight. The digital photograph of SF/Lignin composite film with the square size in $3 \times 3 \text{ cm}^2$. By various the amount of lignin between

0.25, 0.50, 1, and 1.5%(w/v) were indicated, as shown in Figure 100. After added the lignin all the composite films were exhibited an increasing brownish color that can be assumed the successful fabrication of the composite film also still transparency, which can be seen clearly through the background. While applying the mechanic force to the composite films by folding and rolling and then released the mechanic force. All the films can be deformed and returned the shape to the same initial state, which confirmed that the flexibility. However, the thickness of composite films was increased when added more lignin between 0.25, 0.50, 1, and 1.5%(w/v). The thickness was about 285 \pm 0.09, 286 \pm 0.04, 287 \pm 0.05, and 289 \pm 0.03 µm, respectively. All the details were summarized in Table 14.

In order to make the discussion more scientific and support the result of physical properties (optical property) of the SF/Lignin composite film were analyzed by using a UV-Vis spectrophotometer. For understanding the interaction of light with materials, this was definitely essential tool. Therefore, the optical transmittance of SF film and four various amounts of lignin powder loading at 0.25, 0.50, 1, and 1.5%(w/v) in the range of 350-800 nm was shown in Figure 101. By increasing amount of lignin, which caused all the composite films were decreased into the light transmission in the visible region of the spectrum. Incidentally, all composites exhibited the same physical properties. For the pristine SF film and four various amounts of lignin powder loading at 0.25, 0.50, 1, and 1.5%(w/v), respective.



Figure 100 Digital photographs of SF/Lignin before & after folding and rolling

SF/Lignin	Digital	Color &	Surface	Flexibility	Thickness
%(w/v)	photographs	Transparent	morphology	property	(µm)
0.25		Brown & Transparent	Smooth	Flexible	285 ± 0.09
0.50		Brown & Transparent	Smooth	Flexible	286 ± 0.04
1		Brown & Transparent	Smooth	Flexible	287 ± 0.05
1.5		Brown & Transparent	Smooth	Flexible	289 ± 0.03

Table 14 Summarization of physical property of SF composite films with various amounts of lignin



Figure 101 The optical transmittance of SF film and SF/Lignin composite films

4.2.3.2.2. The chemical structural characterization and phase identification of SF/Lignin composite film

Besides the morphological study, the functional groups and chemical bonding characteristics were analyzed by ATR-IR in the range of wavenumber 4000-550 cm⁻¹. For molecular structure characterization of the SF/Lignin composite film, the ATR-IR spectra of SF/Lignin composite film as shown in Figure 102. All peaks were found to be similar to those achieved with the SF film as described. Consequently, the broad band at 3286 cm⁻¹ is explained by the stretching vibration of the overlap of O-H (*v*O-H) and N-H (*v*N-H), which can be identified as the characteristic peaks of the silk structure. There are three absorption peaks around 1620 cm⁻¹, 1518 cm⁻¹ and 1234 cm⁻¹. These peaks are characteristic of C=O stretching vibration (*v*C=O; amide I), C-N stretching vibration (*v*C-N; amide II) and C-N bending vibration (*v*C-N; amide III), respectively.

Therefore, the absorption peak at 1234 cm⁻¹ was attributed to the β -sheet configuration. Due to the relatively lower amount of lignin powder added in comparison to the SF matrix, the IR peaks assigned to lignin were not identified after the addition of lignin (151). This clearly demonstrated the lignin within the SF matrix. However, the addition of lignin neither affected the principal functional groups of the SF, as shown in the FT-IR spectra (152).

The XRD pattern of SF/Lignin composite film was analyzed by X-ray diffraction (XRD). The data was collected over angular range of two theta (2θ) about 10-50° with a step size of 0.02 ° as shown in Figure 103. The pattern only displayed the significant peaks at 2 θ of roughly 12° and 20°, which corresponded to the Silk I structure (random coil content) and Silk II crystal structure (β -sheet content) within the silk fibroin, respectively (127). Moreover, the peaks correlated with the molecular vibration of lignin most likely coincided with many of the strong peaks of the SF matrix. This was required to accommodate the fact that composites often contain a heterogeneous structure, with varying degrees of crystallinity and different phases distributed throughout. This heterogeneity was difficult to deconvolute and interpret, resulting in complex XRD patterns. However, the XRD results can be confirmed that the SF/Lignin composite film was successfully fabricated.



Figure 102 ATR-IR spectra of SF film and SF/Lignin composite films



Figure 103 XRD pattern of SF film and SF/Lignin composite films

4.2.3.3. The electrical output performance of SF/Lignin composite films as charge trapping layer for M-TENG device

Briefly, the SF/Lignin composite films as charge trapping layer for M-TENG was fabricated in the form of a VCS mode. The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribo-material pair movement during the VCS process. The SF/MgAI LDH NS and SF/Lignin composite films were cut into 3 x 3 cm², respectively and the AI tape was used as an electrode with Cu wire connections as shown in Figure 104. An oscilloscope and a DMM were used to measure the electrical output of pure SF film and SF/Lignin composite films (SF-based/M-TENG). The discussion concentrated on the $V_{\rm oc}$, $I_{\rm SC}$ and $P_{\rm max}$ for SF-based/M-TENG device under VSC mode. Furthermore, this section first discussed the working mechanism of the M-TENG device in order to support the electrical performance results for further multilayer structure design. As shown in Figure 105 and 106. The SF film obtained the same V_{oc} and I_{sc} of 63 V and 481 µA as mentioned above. However, by adding the lignin powder in the SF matrix, which is provided in a significant improvement in electricity generation. As the lignin powder content increased to 0.25%(w/v), the V_{oc} and I_{sc} signals also increased significantly. It provided about 96 V, and 656 μ A, respectively. The result was provided the highest V_{oc} and $I_{\rm SC}$ at 0.25%(w/v) of lignin powder content. Nevertheless, by increasing the lignin powder content to 0.5, 1, and 1.5%(w/v) both the V_{oc} and I_{sc} signals were decreased to 87, 73, and 67 V, and 630, 580, and 562 µA, respectively. Due to the molecular structure of lignin contained the hydroxyl group (-OH) in phenol (153). Thus, the highly polar due to significant electronegativity difference between oxygen and hydrogen. The oxygen atom and hydrogen atom are partially negative and partially positive, respectively. This polarity greatly increases the ability of the material to absorb moisture by allowing the hydroxyl groups to form hydrogen bonds with water molecules. When lignin was incorporated into SF composite films the hydroxyl groups could be interacted with water molecules, which is affected to the electrical output performance. The maximum output power P_{max} of SF film and SF/Lignin composite film was also tested under the resistance

range 100 Ω – 100 M Ω . The P_{max} of the SF film was around 100 μ W at 5 M Ω external load resistance, corresponding to a power density of 11.1 μ W/cm². Nevertheless, higher P_{max} of 205 μ W with a power density of 22.8 μ W/cm² was achieved by adding 0.25%(w/v) of lignin powder. The power density of SF was increased 2.1 times as shown in Figure 107. The performance of a typical SF-Based/M-TENG device could be compared with the literature using the electrical output achieved in this work as shown in Table 15.



Figure 104 Schematic diagram of SF-based for M-TENG (1 charge trapping layer)

based on VCS mode



Figure 105 The V_{oc} of SF film and various layer of SF/ML lignin composite film



Figure 106 The $I_{\rm SC}$ of SF film and various layer of SF/ML lignin composite film



Figure 107 The P_{max} of SF/ML lignin 0.25%(w/v) composite film

i

 Table 15 The comparison and output power density with previously reported of SF

 Based S-TENG devices.

Triboelectric materials		Droopen	Flootradaa	V _{oc}	I _{sc}	P_{D}	Rof	
CGL ¹	CGL^2	- Process	Electrodes	(V)	(µA)	(µW/cm ²)	Rel.	
ESSF	PI	Electrospinning	AI	~16	~2.5	~0.43	(154)	
RSSF	PET	Spray-coating	ITO	~213	-	~6.8	(155)	
RSSF	Skin	Casting	Ag NW	~90	~0.06	~2	(156)	
SF/MXene	PDMS	Freeze-drying	ITO	~545	~16.1	~13.25	(157)	
SA	PTFE	Freeze-drying	ITO	~52.8	~5.2	~37	(158)	
ESSF	PCL/GO	Electrospinning	Au	~100	~0.31	~7.2	(159)	
Silk	PTFE	Co-wrapping	SS fiber	~27	~0.43	~0.35	(160)	
RSSF	SNRF	Casting	Mg	~45.2	~0.46	~10.2	(161)	
SF/NFMOF	PDMS	Casting	Al	~120	~9	~128	(162)	

RSSF	RP	Casting	Mg	~55	~0.6	~2.16	(163)
SF/Ag NW	PI	Spray-coating	Cu	~448	~18	~20	(164)
SF/γ-GC	PTFE	Casting	AI	~80	~121	12.5	(165)
CSF	PTFE	Casting	CS	~165	~1.4	~7.2	(166)
SF/3%MgAI	DTEE		A 1	00	000	10.0	This
LDH NS	PIFE	Casting	AI	~80	~600	~18.3	work

Table 15 (Continue) The comparison and output power density with previously reported of SF-Based S-TENG devices.

Note: CGL^{1} (charge generating layer 1), CGL^{2} (charge generating layer 2), V_{oc} (open circuit voltage), I_{sc} (short circuit current), P_{D} (power density), ESSF (electrospun silk fibroin film), RSSF (regenerated silk fibroin film), PI (polyimide), PET (polyethylene terephthalate), ITO (Indium tin oxide), Ag NWs (silver nanowire), SF (silk fibroin), PDMS (polydimethylsiloxane), PTFE (polytetrafluoroethylene), GO (graphene oxide), SS fiber (stainless steel fiber), SNRF (silk nanoribbon), NFMOF (nanoflake metal-organic framework), γ -GC (gamma-glycine), CSF (chitosan silk fibroin), CS (conductive sponge), MgAl LDH NS (magnesium aluminum layer double hydroxide nanosheet).

4.2.3.4. The characterization of multilayer SF/Lignin composite film

The various techniques were used to characterize the SF/Lignin composite film. The morphology of multilayer SF/Lignin composite film was examined by digital imaging.

4.2.3.4.1. The morphological characterization of multilayer SF/Lignin composite film

In the process of SF-Based multilayer structure designed was used SF solution as glue to adhere the SF/MgAI LDH NS and SF/Lignin for 1, 3, and 5 layers, respectively. The digital photograph of SF film with a square size $3 \times 3 \text{ cm}^2$ and a thickness of $341 \pm 0.03 \text{ }\mu\text{m}$ as shown in Figure 108. After applied the mechanical force by folding and rolling. SF-Based flexible multilayer film can be deformed and return to the same initial shape also shown in Table 16.



Figure 108 Digital photographs of SF-Based flexible multilayer film

Number of	Digital	Color &	Surface	Flexibility	Thickness
CTL^1	photographs	Transparent	morphology	property	(µm)
N/A		Brown & Transparent	Smooth	Flexible	286 ± 0.05
1		Brown & Transparent	Smooth	Flexible	574 ± 0.08
3		Brown & Transparent	Smooth	Flexible	857 ± 0.09
5		Brown & Transparent	Smooth	Flexible	1435 ± 0.07

Table 16 Summarization of physical property of SF-Based flexible multilayer film

Note: CTL¹ (charge trapping layer 1)

4.2.3.5. The electrical output performance of SF-based for M-TENG device by various charge trapping layer

Briefly, the SF-based for M-TENG was fabricated in the form of a VCS mode. The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribo-material pair movement during the VCS process. The SF/MgAI LDH NS and SF/Lignin composite films were cut into 3 x 3 cm², respectively and the AI tape was used as an electrode with Cu wire connections. In this work, the numbers of charge trapping layer at 1, 3, and 5 layers was further studied as shown in Figure 109-111. The electrical output of the SF-Based composite film as M-TENG device was tested using an oscilloscope and a digital multimeter to demonstrate the $V_{\rm oc}$ and $I_{\rm sc}$ under VSC mode as shown in Figure 112 and 113. The SF film demonstrated the V_{oc} and I_{sc} of 63 V, 481 μ A respectively. According to the SF/MgAI LDH NS composite film at 3%(v/v) was an optimum condition that provided the highest V_{oc} and I_{sc} of 80 V, 600 μ A respectively. By inserting of 1 charge trapping layer was obtained the highest V_{oc} and I_{sc} of 96 V, 656 μ A respectively with the addition of more layers, which could be improved the electrical performance. Following to the charge carriers as electron could be trapped by the charge trapping layers and their recombination could be avoided (167). In this way, the lifespan of the free charge carriers that could be contributed to the electrical current was increased. However, the increasing numbers of charge trapping layers that were inserted could actually work as an obstruction to the mobility of the charge carriers, by increasing their scattering and decreasing their mobility. As a result of the lower mobility, the effective conductivity is reduced, which resulted in a lower electrical output as the charge carriers were less efficient at moving throughout the device. Thus, in this work the charge trapping layer was inserted to 3, and 5 layers. The $V_{\rm oc}$ and $I_{\rm sc}$ signals were also significantly decreased of 92, 88 V and 584, 542 µA respectively. Therefore, the overall electrical output of the M-TENG can be decreased by adding more charge trapping layers. (168).

The P_{max} of SF-Based composite film with inserting 1 charge trapping layer, that was also tested under the resistance range 100 Ω – 100 M Ω . The P_{max} of the SF-Based composite film with inserting 1 charge trapping layer was around 205 μ W at 5 M Ω external load resistance, corresponding to a power density of 22.8 μ W/cm² as was achieved. The power density of SF-Based composite film with inserting 1 charge trapping layer was increased 1.2 times, which was compared to SF/MgAI LDH 3%(v/v) composite film without inserting charge trapping layer as shown in Figure 114.



Figure 109 Schematic diagram of SF-based for M-TENG (1 charge trapping layer) based on VCS mode



Figure 110 Schematic diagram of SF-based for M-TENG (3 charge trapping layers)



Figure 111 Schematic diagram of SF-based for M-TENG (5 charge trapping layers) based on VCS mode



Figure 112 The V_{oc} of SF-Based composite film with various charge trapping layer



Figure 113 The $I_{\rm SC}$ of SF-Based composite film with various charge trapping layer



Figure 114 The P_{max} of SF-Based composite film with optimum condition

4.2.3.6. The practical application of SF composite films as M-TENG

device

For integration of the SF-Based composite film with inserting 1 charge trapping layer into real devices (SF/M-TENG), it is essential to convert its AC output signal to DC. The SF/M-TENG was connected to a rectifier bridge to achieve this conversion. The resulting DC voltage (V_{DC}) was approximately 40 V and the DC current (I_{DC}) was approximately 100 µA. These electrical output signals as shown in Figure 115. In addition, the stability of the waveform of the I_{DC} was evaluated and confirmed, as shown in Figure 116. The stability of the I_{DC} output indicates the reliability of the SF/M-TENG for a consistent power supply in a practical application. In conclusion, the AC output of the SF/M-TENG was successfully converted to a stable DC signal using a rectifier bridge. This demonstrates the device's the device's practical application. The stability of the DC output also confirms its reliability as a power source for small electronic devices.



Figure 116 The I_{DC} stability signal of SF-M-TENG

To evaluate the long-term stability of the SF/M-TENG, the output voltage stability waveform was analyzed and is presented in Figure 117. Over a period of 1000 seconds, the waveform demonstrated good stability over time. The waveform exhibited characteristics typical of alternating current (AC) voltage with both positive and negative voltage signals. Thus, the peak positive voltage reached to 95 V, while the peak negative voltage was -95 V. This was symmetrical behavior suggested a consistent performance in generating AC voltage, which is crucial for applications requiring reliable and stable power output. The analysis of the $V_{\rm OC}$ stability waveform for SF/M-TENG as mentioned above, which indicated its strong performance in terms of stability and AC voltage generation. These properties underscore the material's potential for long-term, stable use in various electronic and energy harvesting applications. To evaluate the practical application potential of the SF/M-TENG was developed in this work, its chargeability was measured by connecting it to a bridge diode. The chargeability was tested with capacitors of various values 0.22 µF, 0.33 µF, 2.2 µF, and 3.3 µF. As shown in Figure 118. The 0.22 µF capacitor showed remarkable chargeability, reaching a maximum voltage of approximately 4.5 V within approximately 10 seconds. The efficiency of the SF-M-TENG in rapidly storing electrical energy is further enhanced by this rapid charging capability. On the other hand, capacitors with values of 0.33 µF, 2.2 μ F and 3.3 μ F did not succeed in charging to a significant extent within the same 10 second time interval. This study was established the potential of the SF/M-TENG for real applications and demonstrated its ability to serve as a reliable and efficient power source in various practical applications.



Figure 117 The V_{oc} stability waveform measurement of SF-M-TENG depending on the



Figure 118 The chargeability of SF-M-TENG with various capacitors

In addition, the frequency is also an extremely significant point. As shown in Figure 119, the V_{oc} was tested with a mechanical energy applied at a frequency between 3 and 7 Hz. However, at the lowest frequency of 3 Hz, the V_{oc} of SF-Based composite film with inserting 1 charge trapping layer about 43 V. The V_{oc} was higher at 74 V as the frequency increased to 5 Hz. As the frequency steadily increases up to 7 Hz, the electrical output was increased to approximately 95 V. These values are higher than those obtained at lower frequencies.



Figure 119 the $V_{\rm oc}$ of SF-M-TENG at various frequencies from 3 to 7 Hz

Additional testing was completed using a specially designed enclosed chamber to investigate the sensitivity of the SF/M-TENG when placed in a high humidity ambient. These tests were performed under varying humidity conditions as shown in Figure 120. The humidity ranged from 30% to 100% relative humidity (RH). The open circuit voltage (V_{oc}) of the SF/M-TENG decreases significantly with increasing humidity. In particular, the V_{oc} drops from approximately 95 V at 30% relative humidity to approximately 14 V at

100% relative humidity. This trend is further detailed in Figure 121, which shows the progressive decrease in the V_{oc} with increasing RH. The SF/M-TENG was tested under various environmental conditions to assess its humidity sensitivity and durability. Initially, the device provided the V_{oc} of approximately 95 V at 30% relative humidity (RH). This is referred to as the dry state. Nevertheless, when the environment was changed to a high humidity condition of approximately 100% RH, the $V_{\rm oc}$ signal rapidly dropped to approximately 14 V. The device was re-dried at 60°C for 24 hours to test recoverability, as shown in Figure 122. After this process, the V_{oc} was restored to approximately 90 V, which was insignificantly different from the initial dry state. That was indicated after the exposure to high humidity and subsequent redrying, the SF/M-TENG could be recovered its electrical performance. Further durability tests involved performing the device to repeated wet and re-dried cycles. It is notable that after 30 cycles, the device was still generating a $V_{\rm oc}$ of approximately 77 V, as shown in Figure 123. That was demonstrated the resilience and potential of the device for practical applications, as it retains significant performance even after several cycles of wet and dry. However, it was found that after more than 30 cycles of wet and dry. Thus, the SF/M-TENG began to lose flexibility and began to crack, as shown in Figure 124. For the long-term stability of the SF/M-TENG, the output voltage stability waveform was analyzed and presented in Figure 125. The over a period of 1000 seconds, the waveform demonstrated good stability over time after dry and re-dry process. The waveform shown characteristics typical of alternating current (AC) voltage with both positive and negative voltage signals. Thus,

alternating current (AC) voltage with both positive and negative voltage signals. Thus, the peak positive voltage reached to 77 V, while the peak negative voltage was -77 V. This was symmetrical behavior suggested a consistent performance in generating AC voltage, which is crucial for applications requiring reliable and stable power output. In conclusion, while the SF/M-TENG exhibits significant potential for practical applications due to its ability to recover V_{oc} after re-drying, its mechanical durability is compromised after extensive cycling. Future improvements could focus on enhancing the mechanical robustness to extend the device's operational lifespan under varying environmental conditions.



Figure 120 The digital image of the closed chamber with different humidity conditions



Figure 121 The $V_{\rm OC}$ signal of SF/M-TENG as a function of humidity conditions (%RH)



Figure 122 The digital photograph of SF/M-TENG under wet, and re-dry process



Figure 123 The $V_{\rm oc}$ signal of SF/M-TENG after various cycles of wet and re-drying

process



Figure 124 Digital photographs of multilayer SF composite film after dry and re-dry



Figure 125 The $V_{\rm oc}$ stability waveform measurement of SF/M-TENG at 30th re-dried

4.3. Bacterial cellulose (BC) system

4.3.1. BC composite film as charge generating layer

Bacterial cellulose films are biopolymers that are produced by certain bacteria, specifically *Acetobacter* genus, for example; *A. xylinum* (75). This type of cellulose is chemically identical to plant cellulose. However, it is distinguished by its high purity, unique nanostructure and superior physical and mechanical properties. The BC film was firstly chosen to be composited with MgAl LDH NS as charge generating layer for the fabrication of the S-TENG device. For the structural design an additional layer of lignin is added to the intermediate layer as charge trapping layer for the fabrication of the M-TENG. The results and discussion are reported by beginning with the characterization of BC composite films, followed by BC films, MgAl LDH NS, lignin powder and BC composite film, respectively. The morphological characterization was studied by SEM. The chemical structural characterization and phase identification were confirmed by IR, Raman and XRD techniques respectively.

4.3.1.1. The characterization of BC film

The various techniques were used to characterize the BC film. The morphology of SF film was examined by digital imaging and SEM techniques. In addition, ATR-IR, and XRD were used for chemical structural characterization and phase identification.

4.3.1.1.1. The morphological characterization of BC film

After preparation of BC slurry as mentioned in chapter 3.2.4. Briefly, by mixing the BC slurry with glycerin and stirred continuously for 10 minutes at 65°C to degases. Then poured it's into a tray and dried in the hot air oven at 50°C overnight to get the BC film. After applied mechanical force by folding and rolling. BC film can be deformed and return to the same initial shape as shown in Figure 126a-d. The digital photograph of BC film with a square size $3 \times 3 \text{ cm}^2$ and a thickness of $341 \pm 0.03 \mu \text{m}$. After the fabrication of SF film via the casting method. The surface of the BC film appears smooth at low magnification about 500X as shown in Figure 126e but reveals

detailed nanofiber interactions at higher magnification about 50kX as shown in Figure 126f. The images show a highly entangled network of nanofibers with diameters about 17 \pm 5 µm. This network structure was characteristic of bacterial cellulose and contributed to its high surface area and porosity (75, 79). The SEM image shown the dense and interconnected of nanofiber networks, which provided a robust and flexible matrix. Consistent mechanical properties were obtained throughout the film due to the uniform distribution of nanofibers. The nanofibers are randomly oriented, which was typical for BC fabricated under the conditions of fabrication process.



Figure 126 Digital photo of BC film (a) flexibility of BC film (b-d), SEM image of surface morphology of BC film at 500X (e) and 50kX (f) magnification

4.3.1.1.2. The chemical structural characterization and phase identification of BC film

The functional groups and chemical bonding characteristics were analyzed by ATR-IR in the range of wavenumber 4000-550 cm⁻¹ as shown in Figure 127, which was illustrated characteristic peaks corresponding to the functional groups present in BC film. The broad absorption band centered around 3348 cm⁻¹ is attributed to the O-H stretching vibrations (vO-H) of hydroxyl groups, while the band at 1649 cm⁻¹ is attributed to the O-H bending vibration (δ -OH) of absorbed water. The peak at 2900 cm⁻¹ corresponded to the C-H stretching vibration (vC-H) in the cellulose backbone. The peak at 1420 cm⁻¹ corresponded to the CH₂ bending vibration (δ CH₂) and the C-O-C stretching vibrations (vC-O-C) between 1105 cm⁻¹ corresponded to the β -1-4-glycosidic linkages between glucose units, which further confirmed the cellulose structure (75). Following to the list of absorption peaks for BC film was demonstrated in the table 17 and the IR results was confirmed the chemical functional group of BC film.

The XRD pattern of BC film was analyzed by X-ray diffraction (XRD). The data was collected over angular range of two theta (2 θ) about 10-50° with a step size of 0.02°. The XRD analysis confirms the high crystallinity of bacterial cellulose films as shown in Figure 128. The pattern shown distinct peaks at 2 θ values of approximately at 14.7°, 16.6°, and 22.6°, which corresponded to (110), (110), and (200) that are characteristic of cellulose I (169), the crystalline form of cellulose produced by bacteria. The sharpness and intensity of these peaks indicate a well-ordered crystalline structure.

Wavenumber (cm ⁻¹)	Characteristic bonds
3348	-OH stretching vibration
2900	C-H stretching vibration
1649	-OH bending vibration
1420	C-H bending vibration
1105	C-O-C stretching vibration

Table 17 ATR-IR spectral data of BC film



Figure 128 XRD pattern of BC film

4.3.1.2. The characterization of BC/MgAI LDH NS composite films as charge generating layer

The various techniques were used to characterize the SF/MgAI LDH NS composite film. The morphology of SF/MgAI LDH NS composite film was examined by digital imaging, SEM, and EDS techniques. In addition, ATR-IR, Raman, and XRD were used for chemical structural characterization and phase identification.

4.3.1.2.1. The morphological characterization of BC/MgAl LDH NS composite films

The digital photograph of BC/MgAl LDH NS composite film with the square size in 3×3 cm². By various the amount of MgAl LDH NS between 0.25, 0.5, 1, 1.5, 3, and 6%(v/v) were observed, as shown in Figure 129. After added the MgAl LDH NS, the color of all the composite films were not different from the BC film also still translucent, that were visible through the background. While applied the mechanic force to the composite films by folding and rolling and released the mechanic force. All the composite films can be deformed and returned the shape to the same initial state, which confirmed that the flexibility. Furthermore, the thickness of composite films was slightly increased when added more MgAl LDH NS between 0.25, 0.5, 1, 1.5, 3, and 6%(v/v). The thickness was about 343 ± 0.05 , 343 ± 0.02 , 344 ± 0.08 , 345 ± 0.03 , 347 ± 0.04 , and 349 ± 0.07 µm, respectively. All the details were summarized in Table 18.

The morphological of BC/MgAI LDH NS composite film was analyzed by SEM technique at the same 50kx magnification as shown in Figure 130. The SEM images shown a highly entangled network of nanofibers with diameters about 17 ± 5 nm. This network structure was characteristic of bacterial cellulose and contributed to its high surface area and porosity (75, 79). The SEM image shown the dense and interconnected of nanofiber networks, which provided a robust and flexible matrix. Consistent mechanical properties were obtained throughout the film due to the uniform distribution of nanofibers. According to the BC/MgAI LDH NS composite film after added with the various amounts of MgAI LDH NS (0.5, 1.5, and 6%(v/v)). In addition, the micron-sized of MgAI LDH NS were embedded between each bacterial cellulose fiber.
In the increased condition, these are slightly agglomerated as shown in the inset circle in Figure 130b-d. The energy dispersive spectroscopy (EDS) analysis was further used to confirm the elemental components of MgAI LDH NS on the surface of BC/MgAI LDH NS composite film. The result confirmed the carbon (C), oxygen (O), magnesium (Mg) and aluminum (AI). Thus, the elemental index and mapping results of C, O, Mg and AI were represented red, blue, yellow, and orange color, respectively. The content of elements was determined by reporting the weight percentage and atomic percentage as shown in the inset table in Figure 131-133. Due to their negligible concentration compared to the amount of BC matrix, the Mg and AI elements could not be detected at 0.5%(v/v) of loading as shown in Figure 131. The percentage of Mg and AI elements was begun to be detectable at 1.5%(v/v) of loading and then the percentage of Mg and AI was further increased as the loading was increased to 6%(v/v). Therefore, the confirmation of Mg and AI identification can be accomplished by EDS analysis.





Figure 129 Digital photographs of BC/MgAI LDH before & after folding and rolling

BC/MgAl	Digital	Color &	Surface	Flexibility	Thickness
LDH (%wt)	Photographs	Transparent	morphology	property	(µm)
0.25		White & Translucent	Smooth	Flexible	343 ± 0.05
0.50		White & Translucent	Smooth	Flexible	343 ± 0.02
1		White & Translucent	Smooth	Flexible	344 ± 0.08
1.5		White & Translucent	Smooth	Flexible	345 ± 0.03
3		White & Translucent	Smooth	Flexible	347 ± 0.04
6		White & Translucent	Smooth	Flexible	349 ± 0.07

Table 18 Summarization of physical property of BC composite films with various amounts of MgAI LDH



Figure 130 SEM image of surface morphology of BC film (a), BC/MgAI LDH NS 0.5%(v/v) (b), 1.5%(v/v) (c), and 6%(v/v) (d) at 50kX magnification



Figure 131 EDS spectrum and Elemental mapping of BC/MgAI LDH NS 0.5%(v/v)



Figure 132 EDS spectrum and Elemental mapping of SF/MgAI LDH NS 3%(v/v)



Figure 133 EDS spectrum and Elemental mapping of SF/MgAI LDH NS 6%(v/v)

4.3.1.2.3. The chemical structural characterization and phase identification of BC/MgAI LDH NS composite film

The functional groups and chemical bonding characteristics were analyzed by ATR-IR in the range of wavenumber 4000-550 cm⁻¹ as shown in Figure 134, which was illustrated characteristic peaks corresponding to the functional groups present in BC/MgAI LDH NS composite film. The broad absorption band around 3348 cm⁻¹ attributed to the O-H stretching vibrations (vO-H) of hydroxyl groups, while the band at 1649 cm⁻¹ assigned to the O-H bending vibration (*δ*-OH) of absorbed water. The peak at 2900 cm⁻¹ contributed to the C-H stretching vibration (*v*C-H) in the cellulose backbone. The peak at 1420 cm⁻¹ assigned to the CH₂ bending vibration (*δ*CH₂) and the C-O-C stretching vibrations (*v*C-O-C) between 1105 cm⁻¹ corresponded to the β-1-4glycosidic linkages between glucose units, which further confirmed the cellulose structure. Moreover, there was no change in the peak after adding more amounts of MgAI LDH NS between 0.25, 0.5, 1, 1.5, 3, and 6%(v/v). According to the IR results was confirmed the chemical functional group of composite film. The specific absorption peak (Al-O and Mg-O groups) could be the explanation for the bands at around 80-600 cm⁻¹ (38).

The XRD pattern of BC/MgAI LDH NS composite film was analyzed by Xray diffraction (XRD by comparison of BC and MgAI LDH NS). The data was collected over angular range of two theta (2 θ) about 10-50° with a step size of 0.02°. As shown in Figure 135 the XRD analysis was confirmed the high crystallinity of BC films. Thus, the pattern shown distinct peaks at 2 θ values of approximately at 14.7°, 16.6°, and 22.6°, which corresponded to (110), (110), and (200) that are characteristic of cellulose I (169). After adding more amounts of MgAI LDH NS at 0.50 and 1.5 wt% was found that the at the content of 1.5 wt% found the characteristic peak of MgAI LDH of the (003) crystalline planes (38, 108), as shown in the inset pink dot in Figure 134. Furthermore, the XRD results can be confirmed that the BC/MgAI LDH NS composite film was successfully fabricated.



Figure 134 ATR-IR spectra of BC film and BC/MgAI LDH NS composite films



Figure 135 XRD pattern of BC film and BC/MgAI LDH NS composite films

4.3.1.3. The electrical output performance of BC/MgAI LDH NS composite films as charge generating layer for S-TENG device

An oscilloscope and a DMM were used to measure the electrical output of pure SF film and BC/MgAI LDH NS composite films. The discussion concentrated on the V_{oc} , I_{sc} and P_{max} of BC/MgAI LDH NS composite films for S-TENG device.

4.3.1.3.1. The electrical output performance of BC/MgAI LDH NS composite films as charge generating layer for S-TENG device

Briefly, the BC/MgAI LDH NS/S-TENG was fabricated in the form of a VCS mode. The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribomaterial pair movement during the VCS process. The BC/MgAI LDH NS composite films were cut into 3 x 3 cm², and the AI tape was used as an electrode with Cu wire connections as shown in Figure 136. The electrical output of the BC/MgAI LDH NS composite film as S-TENG device was tested using an oscilloscope and a digital multimeter to demonstrate the $V_{\rm oc}$ and $I_{\rm sc}$ under VCS mode. As shown in Figure 137 and 138. The BC film demonstrated $V_{\rm oc}$ and $I_{\rm sc}$ of 25 V and 203 μ A. By adding more amounts of the MgAI LDH NS, which was resulted in a significant improvement in electricity generation. As the MgAI LDH NS content was increased at 0.25, 0.5, 1, and 1.5%(v/v), the V_{oc} and I_{sc} signals also increased significantly. That was provided about 30, 51, 68, and 88 V, and 400, 479, 686, and 884 µA, respectively. According to the result was obtained the highest $V_{\rm oc}$ and $I_{\rm sc}$ at 1.5%(v/v) of MgAI LDH NS content. However, by increasing the MgAI LDH NS content to 3 and 6%(v/v), both the $V_{\rm oc}$ and $I_{\rm sc}$ signals were decreased to 83, and 67 V, and 785, 691 µA, respectively. Due to the agglomerated behavior of the filler particles were reduced the effective surface area, thereby also reduced the interfacial polarization (136). Furthermore, the agglomerated particles generate internal voids and defects which reduce the dielectric properties of the nanosheet (NS) structure and prevent it from producing polarization. Consequently, the dipole orientations are disordered and mutually canceling, producing weak inductive charges and electrical performance (86, 137). The maximum output power P_{max} of BC

film and BC/MgAI LDH NS composite film was also tested under the resistance range 100 Ω – 100 M Ω as shown in Figure 139 and 140. The P_{max} of the BC film was around 37 μ W at 1 M Ω external load resistance, corresponding to a power density of 4 μ W/cm². Nevertheless, higher P_{max} of 542 μ W with a power density of 60.2 μ W/cm² was achieved by adding 1.5%(v/v) of MgAI LDH NS. The power density of BC was increased 15 times.



Figure 136 Schematic diagram of BC/MgAI LDH NS as the S-TENG

based on VCS mode



Figure 137 The V_{oc} of BC film and BC/MgAI LDH NS composite film



Figure 138 The $\rm \it I_{SC}$ of BC film and BC/MgAI LDH NS composite film



Figure 140 The $P_{\rm max}$ of BC/MgAl LDH NS 1.5 wt% composite film

4.3.2. The multilayer structural designed of BC composite film

Before the fabrication of the BC composite film as M-TENG device, the optimum condition for the acquisition of the highest output power of BC/MgAI LDH NS composite film as charge generating layer was obtained. As mentioned above, BC/MgAI LDH NS was achieved the highest V_{oc} and I_{sc} signal 88 V and 884 µA, which was confirmed by adding MgAI LDH NS content of 1.5%(v/v). In addition, the P_{max} was also determined to be 542 µW with a power density of 60.2 µW/cm². For this reason, it could be concluded that the 1.5%(v/v) MgAI LDH NS in SF matrix were used as the charge generating layer. However, the structural design by inserting layer of lignin is added to the intermediate layer as a charge trapping layer. In addition, there are not only discusses the experimental results, but also discusses the scientific understanding the significant role of aromatic lignin structure in the charge trapping layer.

4.3.2.1. The characterization of BC/Lignin composite film as charge trapping layer

The various techniques were used to characterize the BC/Lignin composite film. The morphology of BC/Lignin composite film was examined by digital imaging. In addition, ATR-IR was used for chemical structural characterization.

4.3.2.1.1. The morphological characterization of BC/Lignin composite

film

As mentioned in Chapter 3.4.3.4. Briefly, the mixing of the BC slurry with glycerin, PEG-400, and lignin powder at 0.25, 0.50, 1, and 1.5 wt%, which was stirring continuously for 10 minutes at 65°C. Then pour the mixed slurry into a PS mold and dried in the hot air oven at 50°C overnight. The digital photograph of BC/Lignin composite film with the square size in $3 \times 3 \text{ cm}^2$. By various the amount of lignin powder between 0.25, 0.50, 1, and 1.5 wt% were observed, as shown in Figure 141. After added more amount of the lignin powder all the composite films were demonstrated an increasing brownish color that can be assumed the successful fabrication of the BC/Lignin composite film and the composite film also translucent, that were visible

through the background. While applied the mechanic force to the composite films by folding and rolling and released the mechanic force. This flexibility was confirmed by the fact that all the films could be deformed and returned to the same initial shape. However, the thickness of composite films was slightly increased when added more lignin powder between 0.25, 0.50, 1, and 1.5 wt%. The thickness was about 344 ± 0.09 , 345 ± 0.04 , 347 ± 0.05 , and $349 \pm 0.03 \mu m$, respectively. All the details were summarized in Table 19.



Figure 141 Digital photographs of BC/Lignin before & after folding and roll

BC/ Lignin	Digital	Color &	Surface	Flexibility	Thickness
(%wt)	photographs	Transparent	morphology	property	(µm)
0.25		White & Translucent	Smooth	Flexible	344 ± 0.09
0.50		^L Brown & Translucent	Smooth	Flexible	345 ± 0.04
1		^M Brown & Translucent	Smooth	Flexible	347 ± 0.05
1.5		^D Brown & Translucent	Smooth	Flexible	349 ± 0.03

Table 19 Summarization of physical property of BC composite films with variousamounts of lignin powder

Note: ^LBrown (Light Brown), ^MBrown (Medium Brown), and ^DBrown (Dark Brown)

4.3.2.1.2. The chemical structural characterization and phase identification of BC/Lignin composite film

The functional groups and chemical bonding characteristics were analyzed by ATR-IR in the range of wavenumber 4000-550 cm⁻¹ as shown in Figure 142, which was illustrated characteristic peaks corresponding to the functional groups present in BC/Lignin composite film. The broad absorption band around 3348 cm⁻¹ attributed to the O-H stretching vibrations (ν O-H) of hydroxyl groups, while the band at 1649 cm⁻¹ assigned to the O-H bending vibration (δ -OH) of absorbed water. The peak at 2900 cm⁻¹ contributed to the C-H stretching vibration (ν C-H) in the cellulose backbone. The peak at 1420 cm⁻¹ assigned to the CH₂ bending vibration (δ CH₂) and the C-O-C stretching vibrations (ν C-O-C) between 1105 cm⁻¹ corresponded to the β -1-4-glycosidic linkages between glucose units, which further confirmed the cellulose structure. Moreover, after adding more amounts of lignin powder between 0.25, 0.5, 1, and 1.5 wt%, which was found that the characteristic absorption band of lignin as shown in the highlight-color in Figure 106. The CH₂ asymmetric stretching vibration (ν_{a} CH₂) observed at 2900 cm⁻¹. The C=C stretching vibration (ν C=C) observed at 1594 cm⁻¹ assigned to the skeletal vibration of the aromatic ring (Ar-). The characteristic peaks at 1418 cm⁻¹ attributed to the asymmetric stretching vibration of $-CH_3$ ($v_{as}-CH_3$). According to the IR results was confirmed the chemical functional group of composite film.



Figure 142 ATR-IR spectra of BC film, BC/Lignin composite films and lignin powder

4.3.2.2. The electrical output performance of BC/Lignin composite films as charge trapping layer for M-TENG device

Briefly, the BC/Lignin composite films as charge trapping layer for M-TENG was fabricated in the form of a VCS mode. The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribo-material pair movement during the VCS process. The SF/MgAI LDH NS and BC/Lignin composite films were cut into 3 x 3 cm², respectively and the AI tape was used as an electrode with Cu wire connections as shown in Figure 143. The electrical output of the BC/Lignin composite film as BC-based/M-TENG device was tested using an oscilloscope and a digital multimeter to demonstrate the V_{oc} and I_{sc} under VSC mode. As shown in Figure 144 and 145. The BC film obtained the same V_{oc} and I_{sc} of 25 V and 203 µA as mentioned above. However, by adding the lignin powder, which was provided in a significant improvement in electricity generation. As the lignin

powder content was increased at 0.25 wt%, the V_{\rm oc} and I_{\rm sc} signals also increased significantly. It was provided about 105 V, and 989 µA, respectively. Following to the result was provided the highest $V_{\rm oc}$ and $I_{\rm sc}$ at 0.25 wt% of lignin powder content. Nevertheless, by increasing the lignin powder content to 0.5, 1, and 1.5 wt% both the $V_{\rm oc}$ and $I_{\rm sc}$ signals were decreased to 93, 76, and 62 and 863, 756, and 688 μ A, respectively. Due to the molecular structure of lignin powder contained the hydroxyl group (-OH) in phenol (153). Thus, the highly polar due to significant electronegativity difference between oxygen and hydrogen. The oxygen atom and hydrogen atom in the hydroxyl group are partially negative and partially positive, respectively. This polarity greatly increases the ability of the material to absorb moisture by allowing the hydroxyl groups to form hydrogen bonds with water molecules. In the context of alkaline lignin, the existence of hydroxyl groups contributes to its moisture absorption properties. When lignin powder was incorporated into the Bio-Based composite films the hydroxyl groups could be interacted with water molecules, which was affected the electrical output performance. The Pmax of BC film and BC/Lignin composite film was also tested under the resistance range 100 Ω – 100 M Ω . The P_{max} of the BC film was around 37 μ W at 1 $\text{M}\Omega$ external load resistance, corresponding to a power density of 4 $\mu\text{W/cm}^2$ as mentioned above. Nevertheless, higher P_{max} of 918 μ W with a power density of 102 μ W/cm² was achieved by adding 0.25 wt% of lignin powder. The power density of BC was increased 25.5 times as shown in Figure 146.



Figure 143 Schematic diagram of BC-based for M-TENG (1 charge trapping layer)

based on VCS mode



Figure 144 The V_{oc} of BC film and various layer of BC/ML lignin composite film



Figure 145 The I_{sc} of BC film and various layer of BC/ML lignin composite film



Figure 146 The P_{max} of BC/ML lignin 0.25 wt% composite film

4.3.2.3. The characterization of multilayer BC/Lignin composite film

The various techniques were used to characterize the BC/Lignin composite film. The morphology of multilayer BC/Lignin composite film was examined by digital imaging.

4.3.2.3.1. The morphological characterization of multilayer BC/Lignin composite film

Briefly, in Chapter 3.4.3. Fabrication of BC composite films. In the process of BC-Based multilayer structure designed was used BC slurry as glue to adhere the BC/MgAI LDH NS and BC/Lignin. The digital photograph of BC film with a square size $3 \times 3 \text{ cm}^2$ and a thickness of $341 \pm 0.03 \mu \text{m}$ as shown in Figure 147. After applied the mechanical force by folding and rolling. BC-Based flexible multilayer film can be deformed and return to the same initial shape also shown in Table 20.



Figure 147 Digital photographs of BC-Based flexible multilayer film

Number of	Digital	Color &	Surface	Flexibility	Thickness
CTL^{1}	photographs	Transparent	morphology	property	(µm)
N/A		White & Translucent	Smooth	Flexible	344 ± 0.08
1		^L Brown & Translucent	Smooth	Flexible	691 ± 0.08
3	AMR Banner	^M Brown & Translucent	Smooth	Flexible	1031 ± 0.09
5	<u>N'R</u>	^D Brown & Opaque	Smooth	Flexible	1688 ± 0.12

Table 20 Summarization of physical property of BC-Based flexible multilayer film

Note: CTL¹ (charge trapping layer), ^LBrown (Light Brown), ^MBrown (Medium Brown), and ^DBrown (Dark Brown)

4.3.2.4. The electrical output performance of BC/Lignin composite films as charge trapping layer for M-TENG device

Briefly, the BC-based for M-TENG was fabricated in the form of a VCS mode. The distance gap between the top and bottom materials was fixed by using the screws and nuts. Follow the four springs that were applied to support the tribo-material pair movement during the VCS process. The BC/MgAI LDH NS and BC/Lignin composite films were cut into 3 x 3 cm², respectively and the AI tape was used as an electrode with Cu wire connections. In this work, the numbers of charge trapping layer at 1, 3, and 5 layers was further studied as shown in Figure 148-150. By inserting of 1 charge trapping layer was obtained the highest $V_{\rm oc}$ and $I_{\rm sc}$ of 105 V, 989 μA respectively with the addition of more layers, which could be improved the electrical performance. The electrical output of the BC-Based composite film as M-TENG device was tested using an oscilloscope and a digital multimeter to demonstrate the V_{oc} and I_{sc} under VSC mode. As shown in Figure 151 and 152. The BC film demonstrated the $V_{\rm oc}$ and $I_{\rm sc}$ of 25 V, 203 µA respectively. According to the BC/MgAI LDH NS composite film at 1.5 wt% was an optimum condition that provided the highest $V_{\rm oc}$ and $I_{\rm sc}$ of 88 V, 884 μ A respectively. Following to the charge carriers as electron could be trapped by the charge trapping layers and their recombination could be avoided (144). In this way, the lifespan of the free charge carriers that could be contributed to the electrical current was increased. Nevertheless, the increasing numbers of charge trapping layers that were inserted could actually work as an obstruction to the mobility of the charge carriers, by increasing their scattering and decreasing their mobility. As a result of the lower mobility, the effective conductivity was reduced, which resulted in a lower electrical output as the charge carriers were less efficient at moving throughout the device. Thus, in this work the charge trapping layer was inserted to 3, and 5 layers. The V_{oc} and I_{sc} signals were also significantly decreased of 97, 90 V and 857, 683 µA respectively Therefore, the overall electrical output of the FM-TENG can be decreased by adding more charge trapping layers (168). In addition, to complement the generation of the output performances, the P_{max} of BC-Based composite film with inserting 1 charge trapping layer, that was also

tested under the resistance range 100 Ω – 100 M Ω . The P_{max} of the BC-Based composite film with inserting 1 charge trapping layer was around 918 μ W at 1 M Ω external load resistance, corresponding to a power density of 102 μ W/cm² as was achieved. The power density of BC-Based composite film with inserting 1 charge trapping layer was increased 25.5 times, which was compared to BC/MgAl LDH 1.5%(v/v) composite film without inserting charge trapping layer as shown in Figure 153.



Figure 148 Schematic diagram of BC-based for M-TENG (1 charge trapping layer)

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based on VCS mode



Figure 149 Schematic diagram of BC-based for M-TENG (3 charge trapping layers)



Figure 150 Schematic diagram of BC-based for M-TENG (5 charge trapping layers)

based on VCS mode



Figure 151 The V_{oc} of BC-Based composite film with various charge trapping layer



Figure 152 The $I_{\rm SC}$ of BC-Based composite film with various charge trapping layer



Figure 153 The P_{max} of BC-Based composite film with optimum condition



4.4. The effects of electrons delocalize on the electrical properties and output performance

In this work, the charge trapping layer was prepared by using lignin powder, which included several aromatic rings (153) and provided an area to trap many electrons for a while before being transferred to the charge (170). In order to compare the charge trapping electronic state of SF-Based M-TENG and BC-Based M-TENG, the illustration diagram of the charge trapping mechanism model as shown in Figure 154 and 155. The electrons (pink dots) were generated at the surface of the SF/MgAI LDH NS and BC/MgAI LDH NS composite single layer and trapped in the trap sites. These resulted the deposition of positive charges (blue dots) in the lower AI tape acting as an electrode. This obtained the generation of an electric field between the SF/MgAI LDH NS and BC/MgAI LDH NS composite single layer and AI electrode. In the first step, the electrons were initially trapped in the shallow traps of the SF/MgAI LDH NS and BC/MgAI LDH NS composite single layer. These electrons were moved towards an electrode when they encountered a shallow electric field. However, it was ultimately disappeared through recombination with opposite charges at the electrode, as shown in Figure 154a and 155a. In the next step, the electrons were trapped in the deep trap of the SF/MgAI LDH NS and BC/MgAI LDH NS composite multilayer slowly released from the trap site, which was trapped for a longer time than the potential release rate of the SF/MgAI LDH NS and BC/MgAI LDH NS composite single layer, as shown in Figure 154b and 155b.

As shown in the diagram of the electron trap mechanism in Figure 156. It could be explained by the deep trap charge storage mechanism. Lignin powder is characterized by its abundant composition of functional groups, including methoxy, hydroxy-aliphatic, carboxyl and polyphenolic groups. Its complex and reactive nature is due to these functional groups. Alkaline lignin's structure consists mainly of three primary structural units as Guaiacyl, Syringyl, and *p*-Hydroxyphenyl (171). According to guaiacyl units (G-type) was derived from coniferyl alcohol, which represented a single methoxy group on the aromatic ring. Syringyl units (S-type), which was obtained from sinapyl alcohol, these units consist of two methoxy groups on the aromatic ring. *p*-Hydroxyphenyl units (H-

type), which was derived from p-coumaryl alcohol. These units were lacked methoxy groups on the aromatic ring. The presence of these structural units and functional groups enabled lignin to be a highly versatile and chemically active polymer. It was suitable for many industrial applications, including the production of bio-based materials and energy storage devices. Due to its complex structure allows it to undergo various chemical modifications. The diverse functional groups also play a crucial role in interactions with other materials, which was influenced to the properties such as moisture absorption and electrical conductivity. The significant role of lignin in holding electrons is largely attributed to its structure, which contains numerous aromatic rings. These rings house π -electrons that are delocalized across the entire ring system, rather than being confined to specific atoms. This delocalization allows for resonance stabilization, where the electrons can move freely within the conjugated system (46, 172). In lignin, the aromatic rings create multiple trapping sites. These trapping sites can temporarily hold electrons. This is particularly advantageous in the framework of triboelectric nanogenerator (TENG). As shown in Figure 157, these trapping sites can hold electrons for extended periods of time before being transferred. By holding onto the electrons for a longer period, these trapping sites reduce the probability of recombination of the electrons with opposite charges at the electrodes, thereby ,~+). increasing the efficiency of the TENG (94).



Figure 154 The illustration diagram of charge trapping mechanism model in SF-Based



Figure 155 The illustration diagram of charge trapping mechanism model in BC-Based M-TENG



Figure 156 The schematic diagram of the deep traps storing charge



Mechanism of Electron Delocalization in alkali lignin structure

Figure 157 The ideal mechanism of electron delocalization in lignin structure

CHAPTER 5

CONCLUSIONS

In this work, the biomaterials-based composite consisting of silk fibroin (SF) and bacterial cellulose (BC) was fabricated to serve as the charge generating layer for flexible triboelectric nanogenerators (F-TENG). The approach involved two key strategies:

1. Modification of the composite film as charge generating layer:

To improve the overall efficiency of the TENG by improving the performance of the charge generating layer.

2. Structural design as multilayer TENG:

The implementation of a multilayer structure through the incorporation of a charge trapping layer with the aim of further increasing the electrical performance of the device. Thus, SF and BC films are modified by incorporating various amounts of MgAI LDH NS of 0.5 to 12%(v/v) to find the optimum condition for achieving the highest electrical output. The characteristics of the materials are identified. The functional groups and the fingerprint of MgAI LDH NS and its composites is confirmed by the attenuated total reflection-infrared spectroscopy (ATR-IR) and Raman Spectroscopy. The phase identification and crystal structure are analyzed by X-ray diffraction (XRD). The transmittance of the samples is measured by UV-Vis spectroscopy instrument. The energy gap is determined indirectly by using Tuac's equation. The surface and crosssectional morphology of the samples is studied by scanning electron microscope (SEM). The distribution of MgAI LDH NS in biomaterial composite films is analyzed by Synchrotron radiation X-ray tomographic microscope (SR-XTM). The 3D virtualization is imaged by running Distri software. The effect amounts of MgAI LDH NS and charge trapping layer on the electrical output signal, including the open-circuit output voltage $(V_{\rm OC})$, short-circuit output current $(I_{\rm SC})$ and maximum output power $(P_{\rm max})$ of all the samples are investigated by using oscilloscope and digital multimeter (DMM) in the vertical contact separation mode (VCS).

5.1. The result of preparing the MgAl layer double hydroxide nanosheets (LDH NS)

In this work, the successfully presence of 23 vol% formamide, the rapid synthesis in 10 min of MgAI LDH NS was performed directly. The MgAI LDH NS with a theoretical chemical formula of $[Mg_{0.8}AI_{0.2}(OH)_2] [(NO_3)_{0.2}]_{(s)}$. According to the synthesis of MgAI LDH NS was used of Magnesium nitrate hexahydrate (Mg(NO₃)₂•6H₂O) 0.04 M and Aluminum nitrate nonahydrate (Al(NO₃)₃•9H₂O) 0.01 M as the starting material and formamide as inhibiting reagent *via* co-precipitation method.

5.2. The result of characteristic of MgAl layer double hydroxide nanosheets (LDH NS)

In accordance with the characteristics of MgAI LDH NS, the characterization was divided into morphological, elemental analysis, chemical functional group characterization, and phase identification.

5.2.1. The morphological characterization of MgAI LDH NS

The result of morphology of MgAl LDH NS was observed using digital image and SEM technique. The MgAl LDH NS powder illustrated the white color. In the case of MgAl LDHs, the stacked sample is in the shape of plate-shaped crystals of micron size.

5.2.2. The elemental analysis of MgAI LDH NS

The result of elemental analysis of MgAI LDH NS was observed using the energy dispersive X-ray (EDS) spectroscopy technique. The EDS was a popular microanalysis method for identifying and quantifying the elements contained in a sample. According to the result, which revealed the presence of oxygen (O), aluminum (AI) and magnesium (Mg) in the sampled and then elemental mapping. Thus, the contents of O, Mg, and AI in the sample confirmed by the weight (%) of 63.80%, 24.94, and 11.26 (%), which identified the O, Mg, and AI respectively.

5.2.3. The chemical structural characterization and phase identification of BC film of MgAI LDH NS

The result of chemical functional group of MgAI LDH NS was analyzed using IR spectroscopy technique. The ATR- IR of MgAI LDH NS was observed around 3500-3250 cm⁻¹, which assigned to the stretching vibration of the O-H bond. While the band at 1638 cm⁻¹ was assigned to the bending vibration of O-H bond. Following the two distinct bands were characteristic of the hydroxyl group in water molecule, which generally presented in the interlayer of MgAI LDH NS structure. The peak at 1357 cm⁻¹ was attributed to the vibration of the stretched nitrate ions (NO₃) in the interlayer. The stretching of M-O and O-M-O groups (M = Mg²⁺, Al³⁺) were assigned to the bands at around 800-600 cm⁻¹. The phase purity and crystal structure were determined by XRD analysis and comparison with the JCPDS database. Including to the (003), (006), (012), (015), (018) and (110) crystalline planes and the XRD profiles matched well with JCPDS standard data number 37-0630. In order to confirm the crystal structure, LeBail refinement was carried out using the JANA2006 software. The results were obtained with a consistent MgAI LDH with a hexagonal structure, with well-fitting parameters of Rp = 2.47, Rwp = 3.60 and GOF = 1.46. The lattice parameters were determined to be a = b = 3.045 ± 0.00024 Å and c = 23.337 ± 0.00242 Å. The basal spacing (d₀₀₃) of MgAl LDH corresponding to the intercalation of NO_3^- anions was found to be 0.76 nm. The average crystallite size was also calculated using the Debye Scherrer formula. The result was reported to be 89.0 ± 9.6 nm. While the band gap energy was calculated using the Tauc's equation. The result of MgAI LDH was considered to 5.5 eV. Thus, the IR, XRD and band gap energy results can be confirmed the success of the synthesis of the MgAI LDH NS.

5.3. The result of fabricating the Bio-Based (SF and BC) composite film

In this work, the Bio-Based composite film was studied as SF-Based and BC-Based composite film by incorporating MgAI LDH NS at different content as charge generating layer. On the other hand, lignin powder was studied at different content as charge

trapping layer. The discussion of properties focused on physical properties, surface morphology and chemical structure characterization.

5.4. The result of fabricating the Bio-Based (SF and BC) composite film by incorporating MgAI LDH NS as charge generating layer

According to SF/MgAl LDH NS composite film was further studied with different amount between 0.5, 1, 1.5, 3, 6, and 12%(v/v). All the films could be deformed and returned the shape into initial shaped, which confirmed the flexibility. Furthermore, the thickness of composite films was raised when added more MgAl LDH NS between 0.5, 1, 1.5, 3, 6 and 12%(v/v). The thickness about 283 ± 0.02, 285 ± 0.05, 286 ± 0.08, 286 ± 0.03, 288 ± 0.04, and 0.289 ± 0.07 µm, respectively was obtained.

Furthermore, BC/MgAI LDH NS was also studied with different amount between 0.25, 0.5, 1, 1.5, 3, and 6%(v/v). All the films also confirmed the flexibility. However, the thickness of composite films was increased when added more MgAI LDH NS between 0.25, 0.5, 1, 1.5, 3, and 6%(v/v). The thickness about 283 \pm 0.02, 285 \pm 0.05, 286 \pm 0.08, 286 \pm 0.03, 288 \pm 0.04, and 0.289 \pm 0.07 µm, respectively was obtained. The discussion of properties focused on physical properties, surface morphology and chemical structure characterization.

5.4.1. The morphological characterization of Bio-Based (SF and BC) composite film by incorporating MgAI LDH NS as charge generating layer

In this work, the surface morphology of silk fibroin (SF) film and SF/MgAl LDH NS composite film was examined using SEM at a magnification of 40kX. The SF film exhibited a smooth and uniform surface, indicating good film formation. In contrast, the SF/MgAl LDH NS composite film showed increased roughness and visible filler phases, confirming successful fabrication. Thus, The EDS analysis confirmed the presence of oxygen (O), magnesium (Mg), and aluminum (AI) in the composite film. Elemental mapping showed increasing concentrations of Mg and AI with higher loadings of MgAl LDH NS, detectable from 3%(v/v) and more prominently at 12%(v/v). To evaluate the

dispersion of MgAI LDH NS within the SF matrix, 3D virtualization using SR-XTM was performed. At lower loading 1%(v/v) MgAI LDH NS was sparsely distributed. Higher loadings 3%(v/v) and 12%(v/v) resulted in a homogeneous and well-dispersed morphology, indicating effective integration of MgAI LDH NS into the SF matrix for enhanced composite properties.

To evaluate the surface morphology of BC/MgAI LDH NS composite film was analyzed using SEM at a magnification of 50kX. The SEM images revealed a highly entangled network of nanofibers, characteristic of bacterial cellulose, with diameters around 17 ± 5 nm. This network provided a high surface area and porosity, resulting in a dense, interconnected, robust, and flexible matrix with consistent mechanical properties. Upon incorporating various amounts of MgAI LDH NS (0.5, 1.5, and 6%(v/v)) into the composite film, micron-sized MgAI LDH NS particles were embedded between the bacterial cellulose fibers. At higher loadings, these particles showed slight agglomeration. Energy dispersive spectroscopy (EDS) analysis confirmed the presence of carbon (C), oxygen (O), magnesium (Mg), and aluminum (AI) in the composite film. Elemental mapping showed these elements in red, blue, yellow, and orange, respectively. The weight and atomic percentages of the elements were reported. Mg and AI were undetectable at 0.5%(v/v) loading. EDS analysis thus effectively confirmed the incorporation of Mg and AI in the composite films.

5.4.2. The chemical structural characterization and phase identification of Bio-Based (SF and BC) composite film by incorporating MgAI LDH NS as charge generating layer

In addition to the morphological study, the functional groups and chemical bonding characteristics of the SF/MgAI LDH NS composite film were analyzed using ATR-IR spectroscopy in the wavenumber range of 4000-550 cm⁻¹. The IR spectrum of the composite film exhibited peaks similar to those of the pure SF film. The broadband at 3286 cm⁻¹ attributed to the stretching vibration of overlapping O-H (ν O-H) and N-H (ν N-H) bonds, characteristic of the silk structure. According to amide peaks

assigned to 1620 cm⁻¹, which referred to C=O stretching vibration (ν C=O; amide I), 1518 cm^{-1} , which referred to C-N stretching vibration (vC-N; amide II), and 1234 cm^{-1} , which referred to C-N bending vibration (δ C-N; amide III), attributed to the β -sheet configuration of silk fibroin. There was no change in the amide bands corresponding to the β -sheet configuration after the casting process, confirming the preservation of the silk structure. In conclusion, it was not significant changes in these peaks were observed with varying MgAI LDH NS loadings (0.5 to 12%(v/v)). Additionally, the bands around 800-600 cm⁻¹ were identified as specific absorption peaks for AI-O and Mg-O groups, confirming the presence of MgAI LDH NS in the composite film. Furthermore, The SF/MgAI LDH NS composite film was analyzed by X-ray diffraction (XRD) in the range of 2θ from 10° - 40° . The XRD pattern exhibited distinct peaks at approximately 12° and 20°, indicating the presence of Silk I (random coil) and Silk II (β -sheet) structures, respectively, within the silk fibroin matrix. However, the peaks associated with the MgAI LDH NS were likely overlapping with the strong peaks of the SF matrix. The heterogeneity of the composite, with varying degrees of crystallinity and different phases, resulted in complex XRD patterns that were challenging to deconvolute and interpret, particularly since one of the components (MgAI LDH NS) may have an amorphous nature. Following to the IR and XRD results was confirmed the chemical functional group and crystalline structure of SF/MgAI LDH NS composite film.

For the conclusion of BC/MgAI LDH NS composite film. The ATR-IR spectrum revealed several characteristic peaks. The broadband attributed to O-H stretching vibrations (ν O-H) of hydroxyl groups at 3348 cm⁻¹. Also, the band assigned to O-H bending vibrations (δ -OH) of absorbed water at 1649 cm⁻¹. The peak at 2900 cm⁻¹ corresponded to C-H stretching vibrations (ν C-H) in the cellulose backbone. The peak at 1420 cm⁻¹ assigned to CH₂ bending vibrations (δ CH₂). The peak related to C-O-C stretching vibrations (ν C-O-C), which confirmed β -1-4-glycosidic linkages in cellulose at 1105 cm⁻¹. In conclusion, it was not significant changes in these peaks were observed with varying MgAI LDH NS loadings (0.25 to 6%(v/v)). Additionally, peaks in the range of 800-600 cm⁻¹ likely correspond to Al-O and Mg-O groups, confirming the presence of
MgAI LDH NS in the composite film. Also, the XRD analysis of the BC/MgAI LDH NS composite film, conducted in the 2θ range of 10° - 40° , which compared the diffraction patterns of BC and MgAI LDH NS. The BC film exhibited high crystallinity with distinct peaks at 2θ values of approximately 14.7°, 16.6°, and 22.6°, corresponding to the (110), (110), and (200) planes of cellulose I. Following to the IR and XRD results was confirmed the chemical functional group and crystalline structure of BC/MgAI LDH NS composite film. Upon incorporating MgAI LDH NS, peaks associated with MgAI LDH appeared at $2\theta = 38^{\circ}$, indicating the (003) crystalline plane at a 1.5 wt% loading (highlighted by a pink dot. These results confirm the successful fabrication of the BC/MgAI LDH NS composite films. Following to the IR and XRD results was confirmed the chemical functional group at the successful fabrication of the BC/MgAI LDH NS composite films.

5.5. The result of fabricating the Bio-Based (SF and BC) composite film by incorporating lignin powder as charge trapping layer

According to SF/Lignin composite film was further studied with different amount between 0.25, 0.5, 1, and 1.5%(w/v). After added the lignin powder all the composite films were exhibited an increasing brownish color that can be assumed the successful fabrication of the composite film also still transparency, which can be seen clearly through the background. All the films could be deformed and returned the shape into the initial shaped, which confirmed that the flexibility of the film. However, the thickness of composite films was increased when added more lignin powder between 0.25, 0.50, 1, and 1.5%(w/v). The thickness was about 285 \pm 0.09, 286 \pm 0.04, 287 \pm 0.05, and 289 \pm 0.03 µm, respectively was obtained.

Furthermore, BC/Lignin was also studied with different amount between 0.25, 0.5, 1, and 1.5%(w/v). After added more amount of the lignin powder all the composite films were also demonstrated an increasing brownish color. The composite film was also translucent, that were visible through the background. The flexibility was confirmed by the fact that all the films could be deformed and returned to the same initial shape. However, the thickness of composite films was slightly increased when added more

lignin powder between 0.25, 0.50, 1, and 1.5%(w/v). The thickness was about 344 \pm 0.09, 345 \pm 0.04, 347 \pm 0.05, and 349 \pm 0.03 μ m, respectively was obtained. The discussion of properties focused on physical properties, surface morphology and chemical structure characterization.

5.5.1. Chemical functional group of Bio-Based (SF and BC) composite film by incorporating lignin powder as charge trapping layer

The ATR-IR spectra of the SF/Lignin composite film were analyzed in the range of 4000-550 cm⁻¹ to investigate functional groups and chemical bonding. The IR spectrum of the composite film exhibited peaks similar to those of the pure SF film. The broadband at 3286 cm⁻¹ attributed to the stretching vibration of overlapping O-H (ν O-H) and N-H (vN-H) bonds, characteristic of the silk structure. According to amide peaks assigned to 1620 cm⁻¹, which referred to C=O stretching vibration (vC=O; amide I), 1518 cm⁻¹, which referred to C-N stretching vibration (ν C-N; amide II), and 1234 cm⁻¹, which referred to C-N bending vibration (δ C-N; amide III), attributed to the β -sheet configuration of silk fibroin. There was no change in the amide bands corresponding to the β -sheet configuration, confirming the preservation of the silk structure. Despite the addition of lignin powder, which was present in relatively low amounts compared to the SF matrix, no distinct peaks for lignin were detected. This suggests that while lignin powder is incorporated into the SF matrix, it does not significantly alter the primary functional groups of the silk fibroin. The characteristic peaks of SF remained unchanged across lignin powder loadings of 0.25, 0.5, 1, and 1.5 wt%. The XRD analysis of the SF/Lignin composite film, conducted in the 2θ range of 10° - 40° , revealed significant peaks at approximately 12° and 20°. These peaks correspond to the Silk I structure (random coil) and Silk II crystal structure (β -sheet), respectively. The peaks related to lignin were not distinctly observed due to their overlap with the prominent peaks of the silk fibroin matrix. This overlap is typical in composites with heterogeneous structures, where varying degrees of crystallinity and phase distribution complicate the interpretation of XRD patterns. Despite this, the XRD results confirm the successful fabrication of the SF/Lignin composite film.

For the conclusion of BC/Lignin composite film. The ATR-IR spectrum revealed several characteristic peaks. The broadband attributed to O-H stretching vibrations (ν O-H) of hydroxyl groups at 3348 cm⁻¹. Also, the band assigned to O-H bending vibrations (δ -OH) of absorbed water at 1649 cm⁻¹. The peak at 2900 cm⁻¹ corresponded to C-H stretching vibrations (ν C-H) in the cellulose backbone. The peak at 1420 cm⁻¹ assigned to CH₂ bending vibrations (δ CH₂). The peak related to C-O-C stretching vibrations (ν C-O-C), which confirmed β -1-4-glycosidic linkages in cellulose at 1105 cm⁻¹. Additionally, with the incorporation of lignin powder at 0.25, 0.5, 1, and 1.5% (w/v), characteristic absorption bands of lignin powder were observed. The peak at 2900 cm⁻¹ assigned to CH₂ asymmetric stretching vibration (ν_{as} -CH₂). The peak at 1594 cm⁻¹ assigned to C=C stretching vibration (ν C=C), associated with aromatic ring skeletal vibrations. The peak at 1418 cm⁻¹ attributed to CH₃ asymmetric stretching vibration (ν_{as} -CH₃). In conclusion, The ATR-IR results confirm the presence of both cellulose and lignin functional groups in the composite film.

5.6. The result of fabricating the Bio-Based (SF and BC) composite film as flexible single layer triboelectric nanogenerator (S-TENG)

The electrical output of the Bio-Based (SF and) composite S-TENG was measured and analyzed using an oscilloscope and digital multimeter. Thus, the TENG was periodically mechanical tapped using a linear motor to simulating mechanical stimulation. The V_{oc} and I_{sc} were read and recorded at different frequencies and amplitudes. By measuring the voltage against different load resistances, the power density was calculated.

5.6.1. The result of output performance of SF/MgAl LDH composite film as charge generating layer for flexible single layer triboelectric nanogenerator (S-TENG)

The electrical performance of the SF/MgAl LDH NS composite film, tested as S-TENG device, shown notable improvements with increasing MgAl LDH NS content. Following the SF Film was provided the V_{oc} and I_{sc} of 63 V and 481 µA, respectively. However, with the addition of MgAl LDH NS at 0.5, 1, 1.5, 3, 6 and 12%(v/v) was provided the V_{oc} of 68, 71, 74, 80, 77, and 69 V, respectively and the I_{sc} of 500, 541, 556, 600, 520, and 496 µA, respectively. The Increasing of MgAl LDH NS content led to enhanced the V_{oc} and I_{sc} until 3%(v/v), beyond which agglomeration reduced performance. Also, the P_{max} of SF Film of 100 µW (11.1 µW/cm²) at 5 M Ω load resistance and SF/MgAl LDH NS at 3%(v/v) provided the P_{max} of 165 µW (18.3 µW/cm²), 1.6 times increase in power density.

5.6.2. The result of output performance of SF/Lignin composite film as charge trapping layer for flexible multilayer triboelectric nanogenerator (M-TENG)

The electrical performance of the SF/Lignin composite film, tested as M-TENG device, shown notable improvements with increasing lignin powder content. Following the SF Film was provided the V_{oc} and I_{sc} of 63 V and 481 µA, respectively. However, with the addition of lignin powder at 0.25, 0.5, 1, and 1.5%(w/v) was provided the V_{oc} of 96, 87, 73, and 67 V, respectively and the I_{sc} of 656, 630, 580, and 562 µA, respectively. The Increasing of lignin powder content led to enhance the V_{oc} and I_{sc} until 0.25 wt%, beyond which agglomeration reduced performance. Also, the P_{max} of SF Film of 100 µW (11.1 µW/cm²) at 5 M Ω load resistance and SF/Lignin at 0.25%(w/v) provided the P_{max} of 205 µW (22.8 µW/cm²), 2.1 times increase in power density.

5.6.3. The result of output performance of BC/MgAI LDH composite film as charge generating layer for flexible single layer triboelectric nanogenerator (S-TENG)

The electrical performance of the BC/MgAI LDH NS composite film, tested as S-TENG device, shown notable improvements with increasing MgAI LDH NS content. Following the BC Film was provided the V_{oc} and I_{sc} of 25 V and 203 μ A,

respectively. However, with the addition of MgAI LDH NS at 0.25, 0.5, 1, 1.5, 3, and 6%(v/v) was provided the V_{oc} of 30, 51, 68, 88, 83, and 67 V, respectively and the I_{sc} of 400, 479, 686, 884, 785, and 691 µA, respectively. The Increasing of MgAI LDH NS content led to enhanced the V_{oc} and I_{sc} until 1.5 wt%, beyond which agglomeration reduced performance. Also, the P_{max} of BC Film of 37 µW (4 µW/cm²) at 1 M Ω load resistance and BC/MgAI LDH NS at 1.5%(w/v) provided the P_{max} of 542 µW (60.2 µW/cm²), 15 times increase in power density.

5.6.4. The result of output performance of BC/Lignin composite film as charge trapping layer for flexible multilayer triboelectric nanogenerator (M-TENG)

The electrical performance of the BC/Lignin composite film, tested as M-TENG device, shown the notable improvements with increasing lignin powder content. Following the BC Film was provided the V_{oc} and I_{sc} of 25 V and 203 µA, respectively. However, with the addition of lignin powder at 0.25, 0.5, 1, and 1.5% (w/v) was provided the V_{oc} of 67, 59, 43, and 35 V, respectively and the I_{sc} of 521, 492, 387, and 264 µA, respectively. The Increasing of lignin powder content led to reduce the V_{oc} and I_{sc} , which is the agglomeration performance. Also, the P_{max} of BC Film of 37 µW (4 µW/cm²) at 1 M Ω load resistance and BC/Lignin at 0.25% (w/v) provided the P_{max} of 918 µW (102 µW/cm²), 25.5 times increase in power density.

5.7. The result of fabricating the Bio-Based composite film as flexible multilayer triboelectric nanogenerator (M-TENG)

The electrical output of the Bio-Based composite M-TENG was measured and analyzed using an oscilloscope and digital multimeter. Thus, the TENG was periodically mechanical tapped using a linear motor to simulating mechanical stimulation. The V_{oc} and I_{sc} were read and recorded at different frequencies and amplitudes. By measuring the voltage against different load resistances, the power density was calculated.

5.7.1. The result of output performance of SF composite film for multilayer triboelectric nanogenerator (M-TENG) by various charge trapping layer

The electrical performance of the SF-Based composite film, tested as M-TENG device. Following the SF Film was provided the V_{oc} and I_{sc} of 63 V and 481 µA, respectively. However, with the optimum condition of MgAl LDH NS at 3%(v/v) was provided the V_{oc} and the I_{sc} of 80 V and 600 µA respectively. By adding 1 charge trapping layer (SF/Lignin 0.25 wt%) resulted in the highest V_{oc} and I_{sc} of 96 V and 656 µA, respectively. The improving electrical performance by trapping layers led to decreased V_{oc} and I_{sc} signal. At the 3 layers was provided the V_{oc} and I_{sc} of 92 V and 584 µA, respectively and 5 layers was provided the V_{oc} and I_{sc} of 88 V and 542 µA, respectively. In conclusion, by increasing more layers was obstructed charge carrier mobility, reducing overall electrical output. The P_{max} of the SF-based/M-TENG was tested from 100 Ω to 100 M Ω , the maximum power of 205 µW at 5 M Ω load and a power density of 22.8 µW/cm², which was 2.1 times higher than the SF-Based film without charge trapping layers.

5.7.2. The result of output performance of BC composite film for multilayer triboelectric nanogenerator (M-TENG) by various charge trapping layer

The electrical performance of the BC-Based composite film, tested as M-TENG device. Following the BC Film was provided the V_{oc} and I_{sc} of 25 V and 203 μ A, respectively. However, with the optimum condition of MgAI LDH NS at 1.5 wt% was provided the V_{oc} and the I_{sc} of 88 V and 884 μ A respectively. By adding 1 charge trapping layer (BC/Lignin 0.25 wt%) resulted in the highest V_{oc} and I_{sc} of 105 V and 989 μ A, respectively. The improving electrical performance by trapping layers led to decreased V_{oc} and I_{sc} signal. At the 3 layers was provided the V_{oc} and I_{sc} of 97 V and 857 μ A, respectively and 5 layers was provided the V_{oc} and I_{sc} of 90 V and 683 μ A, respectively. In conclusion, by increasing more layers was obstructed charge carrier mobility, reducing overall electrical output. The P_{max} of the SF-Based composite film with

1 charge trapping layer was tested from 100 Ω to 100 M Ω , the maximum power of 918 μ W at 1 M Ω load and a power density of 102 μ W/cm², which was 25.5 times higher than the BC-Based film without charge trapping layers.



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