

Sustainable Energy Harvesting: Structural Analysis Approaches in Zeolitic Imidazolate Framework- Based Triboelectric Nanogenerators

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by

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Sustainable Energy Harvesting: Structural Analysis Approaches in Zeolitic Imidazolate Framework-Based Triboelectric Nanogenerators

Abstract

The rising demand for sustainable, autonomous energy systems has accelerated research into technologies that convert ambient mechanical stimuli into electricity. This study examines two ZIF-8 and ZIF-67-based triboelectric nanogenerators, noted for their simple architecture, low cost, and compatibility with diverse materials.

A hybrid-mode TENG utilizing ZIF-8 was designed for marine applications, where thin films of ZIF-8 were deposited on copper tape and coupled with a polystyrene counterpart. The device combined vertical contact-separation and lateral sliding modes to harness multidirectional water wave motion. It demonstrated a peak voltage of 195 V open circuit and a power density of 803 mV/m² under a 2 Hz actuation frequency. Moreover, our original TENG design based on ZIF-8 achieved a peak power density of ≈ 803 mW/m², surpassing the 600–700 mW/m² range typically reported for MOF-enhanced devices in the literature, underscoring both its novel architecture and excellent energy-harvesting performance. Together, the dual-mode operation ensures that both the vertical and horizontal components of ocean-wave motion are harnessed: the contact mode delivers high instantaneous voltages through normal compression, while the sliding mode capitalizes on tangential motion to increase charge throughput and cumulative voltage. These results offer a range of power applications including environmental sensors, wireless communication modules, status LEDs, real-time clocks, and intermittent actuator bursts, demonstrating a seamless integration of multi-axis mechanical energy harvesting with practical power management for marine sensing and communication systems.

In parallel, ZIF-67 was employed in a contact-mode TENG embedded into shoe soles for biomechanical energy harvesting. This study presents an original approach as the first example of integrating an accordion-patterned ZIF-67 thin film on an aluminum substrate into a shoe sole. The aluminum-supported ZIF-67 thin film is projected to power low-power, shoe-embedded wearable electronics (e.g., Bluetooth beacons, inertial sensors, or haptic feedback units) without an external battery, delivering a peak voltage of up to 36 V and a power density of approximately 108 mW/m². This performance is attributed to ZIF-67's higher electron affinity with aluminum electrodes and its enhanced surface interactions.

Additionally, detailed structural characterizations including single-crystal X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were carried out to link film crystallinity, surface morphology, and nanoscale roughness with the observed electrical output. Complementing these experiments, Density Functional Theory (DFT) calculations were used to interrogate the electronic structure and surface charge distribution of both ZIF-8 and ZIF-67 frameworks. The Density Functional Theory (DFT) results reveal that alignment of pore channels along specific crystallographic axes in ZIF-8 and the presence of well-defined grain boundaries in ZIF-67 critically enhance the local surface potential and facilitate charge transfer across the polymer-metal interface. Our spin-coated ZIF-8 films on copper and aluminum exhibited (011) reflections with FWHM values of 0.12–0.15°, closely matching the ~0.14° benchmark reported for ZIF-8 on silicon wafers and displayed a robust and intensity ratio according to literature values. Separately, our ZIF-67 coatings showed peak widths of 0.18–0.22°, which are comparable to but slightly broader than the ~0.16° FWHM documented for spin-coated ZIF-67 on gold substrates, with orientation ratios in line with typical near-unity values reported in prior studies. The combination of experimental and theoretical approaches has verified the central role of microstructural parameters in determining triboelectric performance and aims to establish a solid foundation for the rational design and scalable fabrication of ZIF-based TENGs across diverse energy-harvesting applications.

Keywords: Triboelectric nanogenerator, ZIF-8, ZIF-67, hybrid energy harvesting, marine energy, wearable electronics

Sürdürülebilir Enerji Hasadı: Zeolitik İmidazolat Çerçeve Tabanlı Triboelektrik Nanogeneratörlerde Yapısal Analiz Yaklaşımları

Öz

Sürdürülebilir, özerk enerji sistemlerine yönelik artan talep, ortamdan gelen mekanik uyarıları elektrığe dönüştüren teknolojiler üzerine araştırmaları hızlandırmıştır. Bu çalışma, basit mimarisi, düşük maliyeti ve farklı malzemelerle uyumuyla dikkat çeken iki ZIF-8 ve ZIF-67 bazlı triboelektrik nanojeneratörü (TENG) incelemektedir. Bir yandan, ZIF-8 kullanılarak deniz uygulamaları için hibrit modlu bir TENG tasarlanmıştır. Bu cihazda, bakır bant üzerine ince film olarak yatırılan ZIF-8, polistiren karşı elektrotla birleştirilmiş ve dikey temas-ayırma ile yatay kayma modlarını bir arada kullanabilen çok eksenli su dalgası hareketini dönüştürme yeteneği kazandırılmıştır. 2 Hz tahrik frekansında cihaz, 195 V'luk en yüksek açık devre voltajı ve 803 mW/m² güç yoğunluğu sergilemiştir. Ayrıca, ZIF-8 tabanlı özgün TENG tasarımı, literatürde genellikle 600–700 mW/m² arasında rapor edilen MOF destekli cihazları geride bırakarak ≈ 803 mW/m² tepe güç yoğunluğu elde etmiş ve hem yenilikçi mimarisini hem de mükemmel enerji toplama performansını ortaya koymuştur. Dikey mod, normal baskı sayesinde yüksek anlık voltajlar üretirken; kayma modu, tanjantiyel hareketi kullanarak yük aktarımını ve kümülatif voltajı artırır. Bu sayede, çevresel sensörler, kablosuz iletişim modülleri, durum LED'leri, gerçek zamanlı saatler ve kısa süreli aktüatör patlamaları gibi bir dizi güç uygulamasına olanak tanıyarak, çok eksenli mekanik enerji hasadı ile deniz tabanlı algılama ve iletişim sistemlerinin pratik güç yönetimini kesintisiz bir biçimde bütünleştirir.

Paralel olarak, ZIF-67, biyomekanik enerji hasadı için ayakkabı tabanlarına entegre edilen temas modlu bir TENG'de kullanılmıştır. Bu çalışma, ZIF-67 ince filminin

alüminyum substrat üzerine akordeon biçiminde tasarlanarak ayakkabı tabanına entegre edildiği ilk örnek olmasıyla alanda özgün bir yaklaşım sunmaktadır. Alüminyum destekli ZIF-67 ince filmi, 36 V'a ulaşan tepe voltajı ve yaklaşık 108 mW/m² güç yoğunluğu ile ayakkabı içine gömülü düşük güçlü giyilebilir elektronik cihazları (Bluetooth beacon'lar, ataletsel sensörler veya dokunsal geri bildirim birimleri gibi) harici batarya gerektirmeden besleyebileceğini öngörmektedir. Bu öngörü, ZIF-67'nin alüminyum elektrotlarla daha yüksek elektron afinitesi ve geliştirilmiş yüzey etkileşimine atfedilmektedir.

Ayrıca, ince film kristallliği, yüzey morfolojisi ve nanoskaladaki pürüzlülüğün gözlenen elektriksel çıktıyla ilişkisini ortaya koymak üzere tek kristal X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM) ve atomik kuvvet mikroskobu (AFM) gibi ayrıntılı yapısal karakterizasyonlar gerçekleştirilmiştir. Bu deneysel çalışmaların tamamlayıcısı olarak, her iki ZIF çerçevesinin elektronik yapısını ve yüzey yük dağılımını incelemek için Yoğunluk Fonksiyonel Teorisi (DFT) hesaplamaları yapılmıştır. DFT sonuçları, ZIF-8'de belirli kristalografik eksenler boyunca gözenek kanallarının hizalanmasının ve ZIF-67'de iyi tanımlanmış tane sınırlarının, yerel yüzey potansiyelini önemli ölçüde artırarak polimer-metal ara yüzeyindeki yük iletimini kolaylaştırdığını ortaya koymuştur. Bakır ve alüminyum yüzeylere spin-kaplama yöntemiyle oluşturduğumuz ZIF-8 filmleri, yaklaşık 0,14°'lik referans değeri yakalayan, 0,12–0,15° FWHM değerlerine sahip (011) refleksiyonlar sergileyip literature göre güçlü bir yoğunluk oranı göstermiştir. Bununla birlikte, ZIF-67 kaplamalarımız, altın substratlar üzerinde bildirilen ~0,16° FWHM değerine benzer ancak biraz daha geniş 0,18–0,22° aralığında pik genişlikleri ve önceki çalışmalarda belirtilen yaklaşık birim değerlerine yakın yönelim oranları sergiledi. Deneysel ve teorik yaklaşımların birleşimi, mikro yapısal parametrelerin triboelektrik performansı belirlemedeki merkezi rolünü doğrulamış ve çeşitli enerji hasadı uygulamalarında ZIF bazlı TENG'lerin akılcı tasarımı ile ölçeklenebilir üretimi için sağlam bir temel oluşturmayı amaçlamıştır.

Anahtar Kelimeler: Triboelektrik nanogeneratör, ZIF-8, ZIF-67, hibrit enerji toplama, deniz enerjisi, giyilebilir elektronik

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List of Abbreviations

FBE	Fen Bilimleri Enstitüsü
İKÇÜ	İzmir Kâtip Çelebi University
ORCID	Open Researcher and Contributor ID



List of Symbols

σ	Surface charge density
I_0	Intensity of the incident X-ray beam
I	Intensity of the diffracted X-ray beam
μ	Linear absorption coefficient
ρ	Material density
$U^2 = \langle r^2 \rangle$	Thermal displacement parameter
B	Atomic displacement factor – unit: Å ²
θ	Diffraction angle
λ	X-ray wavelength
φ	Angle between reciprocal lattice vector and equatorial plane
α	Angle between scattering direction and electron acceleration
$E_x c$	Exchange–correlation energy
$v_x c$	Exchange–correlation potential
ψ	Kohn–Sham orbitals
$\Delta\rho(x, y, z)$	Difference in electron density
R	Residual value (Reliability index)
R_w	Weighted residual factor

Chapter 1

Introduction

The rapid advancement of modern technologies, particularly in areas such as the Internet of Things (IoT), artificial intelligence (AI), and human-machine interfaces, has significantly transformed various aspects of human life. These innovations have led to the development of miniaturized, multifunctional, and lightweight electronic devices that play crucial roles in fields such as health monitoring, wearable electronics, and self-powered systems. However, the widespread reliance on conventional batteries to power these devices presents several limitations, including finite lifespans, environmental concerns, and size constraints. Furthermore, while mature power generation technologies such as solar cells, electromagnetic generators (EMGs), and thermoelectric generators (TEGs) offer alternative solutions, their inherent drawbacks make them unsuitable for long-term and sustainable use in compact electronic systems. Addressing this gap requires the development of self-powered devices that are not only flexible and efficient but also environmentally friendly. Nanogenerators, which mechanically harvest energy from ambient surroundings, have emerged as a promising solution for this purpose. Among nanogenerators, two primary types are widely studied: piezoelectric nanogenerators (PENGs) and triboelectric nanogenerators (TENGs). While both systems efficiently convert mechanical energy into electrical energy, TENGs offer superior versatility, cost-effectiveness, and simpler configurations, making them particularly suitable for next-generation electronic devices. Since their introduction by Prof. Z.L. Wang in 2012, TENGs have gained significant attention for their ability to convert mechanical energy into electrical energy through the combined principles of the triboelectric effect and electrostatic induction.

The triboelectric effect occurs when two dissimilar materials come into contact and then separate, resulting in charge transfer due to differences in electron affinity. TENGs utilize this mechanism to create electrical energy, operating across four

primary modes: vertical contact-separation (VCS), single-electrode, freestanding, and lateral sliding. Among these, the VCS mode is particularly favored for its simplicity and effectiveness, minimizing physical wear while maintaining robust performance. Additionally, TENGs are characterized by their wide range of material choices, ease of fabrication, and high output performance, making them highly adaptable for various applications, from powering IoT devices to self-powered sensors and wearable technologies.

The efficiency and performance of TENG devices are closely tied to the selection of materials used as triboelectric layers. Traditional triboelectric materials include polymers, metals, and natural substances, which have been extensively studied. However, researchers have increasingly turned their attention to advanced materials such as metal-organic frameworks (MOFs), which offer unique properties that are well-suited for energy harvesting applications. MOFs, a distinctive class of crystalline porous materials, are composed of metal ions or clusters coordinated with organic ligands, forming highly ordered three-dimensional networks. These materials are celebrated for their exceptional characteristics, including high surface area, tunable porosity, chemical and thermal stability and structural flexibility.

Among MOFs, zeolitic imidazole frameworks (ZIFs) have emerged as particularly promising candidates for TENG applications. ZIFs, a subclass of MOFs, feature a unique combination of large surface area, high crystallinity, adjustable pore sizes, and remarkable thermal and chemical stability. These properties make ZIFs suitable for a wide range of applications, including gas storage, catalysis, sensing, and energy harvesting. Recent studies have demonstrated the potential of ZIFs in TENG devices, with several types, such as ZIF-8, ZIF-7, and ZIF-62, being employed as positive triboelectric layers. Despite these advancements, the full potential of ZIFs in TENGs remains underexplored, particularly in terms of their functionalization and structural optimization.

This research aims to explore the potential of ZIF -MOF based TENGs as an innovative solution to meet the growing energy demands sustainably and efficiently. By leveraging the unique properties of ZIF MOFs, this work seeks to address key challenges in TENG performance, including charge density, energy output, and

environmental adaptability. The ultimate goal is to develop a scalable, cost-effective, and high-performance energy harvesting system capable of powering small electronic devices, such as LEDs, while contributing to a greener and more sustainable energy landscape. This involves rigorous testing to assess the energy generation capacity, efficiency, and reliability of the device under various operational scenarios. By demonstrating the capability to power LEDs, the research highlights the potential for ZIF-MOF-based TENGs to serve as a sustainable energy source for everyday applications. The evaluation process also includes analyzing the device's long-term stability and adaptability to environmental factors such as humidity, temperature, and mechanical wear.

Another significant objective is the optimization of the structural and material properties of ZIF-MOFs to enhance their triboelectric performance. This involves systematic investigations into the effects of ZIF-MOF structural parameters, such as porosity, particle size, and surface functionalization, on charge generation and energy conversion efficiency. The research aims to identify the optimal combination of material properties and fabrication techniques to maximize the device's performance.

Additionally, the research seeks to explore innovative integration methods for ZIF-MOF materials into TENG designs to improve mechanical and electrical properties. This includes developing advanced fabrication processes to ensure uniform material distribution, robust device assembly, and compatibility with flexible or portable device configurations. The outcomes of these efforts aim to establish a blueprint for scalable production of high-performance ZIF-MOF-based TENGs.

This study focuses on the development of a cost-effective TENG device utilizing ZIF-8 and ZIF-67. This thesis makes several key contributions to the field of energy harvesting and triboelectric nanogenerators (TENGs). Firstly, it introduces the novel application of ZIF MOF materials in TENGs, leveraging their exceptional properties such as high porosity, tunable surface chemistry, and structural stability to enhance the device's triboelectric performance. This innovative integration not only addresses existing limitations in conventional TENG designs but also opens new avenues for material-based performance enhancements. Secondly, the research focuses on the development of a scalable TENG capable of powering small electronic devices, such

as LEDs. By designing and fabricating a device that combines efficiency with scalability, this work demonstrates the practical applicability of ZIF MOF-based TENGs in real-world scenarios. The scalability aspect ensures that the device can be adapted for a range of applications, from portable electronics to larger energy systems, contributing to its versatility and utility. Finally, the thesis conducts a comprehensive evaluation of the environmental and economic sustainability of ZIF MOF-based TENGs. This includes assessing the device's life cycle, material recyclability, and overall environmental impact, as well as analyzing the cost-effectiveness of the proposed design. By addressing both the environmental and economic aspects, the research provides a holistic understanding of the potential of ZIF MOF-based TENGs as a sustainable energy solution, aligning with the global push toward greener and more efficient technologies.

As a result, the structure of this thesis is organized into six main chapters, each addressing a specific aspect of the research. Chapter 1(Introduction) provides an overview of the research motivation, objectives, and the key contributions of the study. This chapter sets the context for the thesis and outlines its significance in the broader scope of renewable energy technologies. Chapter 2 (Literature Review) delves into the fundamental principles of triboelectric nanogenerators (TENGs), their operational modes, and the role of materials in enhancing their performance. It also explores the unique properties of ZIF MOF structures and their potential applications in energy harvesting technologies. This chapter establishes the theoretical foundation for the research. Chapter 3 (Methodology) details the experimental and fabrication techniques used in the research. It includes the synthesis and characterization of ZIF MOF materials, preparation of dielectric layers, and the assembly and testing of the TENG devices. This chapter provides a comprehensive guide to the methods employed to achieve the research objectives. Chapter 4 (Results and Discussion) presents the experimental findings, including the performance analysis of ZIF MOF-based TENGs, their energy generation capabilities, and material characterization results. This chapter also includes a detailed discussion on the implications of these findings and their alignment with the research goals. Chapter 5 (Future Work) outlines potential directions for further research, including strategies for enhancing TENG performance, integrating the technology with other systems, and scaling up for larger applications.

Chapter 6 (Conclusions) summarizes the key findings and contributions of the thesis. It reflects on the significance of the research outcomes and their impact on advancing renewable energy technologies.

Ultimately, this research contributes to advancing the field of energy harvesting by combining cutting-edge nanotechnology and material science. By addressing the design, application, and optimization of ZIF-MOF-based TENGs, the study paves the way for the development of practical, efficient, and environmentally sustainable energy solutions that can meet the growing demands of modern society.



Chapter 2

Literature Review

2.1 Triboelectric Nanogenerators (TENGs)

In recent years, the explosive expansion of the Internet of Things (IoT) and wearable electronics has driven urgent demand for miniature, self-sustaining power sources. Triboelectric nanogenerators (TENGs) have emerged as a leading solution, converting ambient mechanical energy such as human motion, water waves, wind, or raindrops into electrical power via coupled contact electrification and electrostatic induction (Niu et al., 2014; Dharmasena et al., 2017). These “nanogenerators” employ nanometer-scale materials to maximize surface charge transfer under mechanical deformation (Kim et al., 2021; Zhang & Ölin, 2020), harvesting energy from diverse sources including walking, breathing, jogging, heartbeats, vibrations, and environmental stimuli (Rahman et al., 2023; Rana et al., 2024).

TENGs are fabricated in various geometries including rectangular, circular, or irregular with lateral dimensions ranging from a few millimeters to several centimeters (Gao et al., 2024; Slater & Tan, 2024) and thicknesses spanning micrometers to millimeters (More et al., 2022; Shao et al., 2023). Electrode areas may vary from square millimeters to multiple square centimeters, with inter-electrode separations adjustable from a few microns up to several millimeters to tune capacitance and output characteristics (Memon et al., 2024; Velpula et al., 2024). Four fundamental operation modes including vertical contact–separation, lateral sliding, single-electrode, and freestanding triboelectric-layer offer design flexibility: contact–separation maximizes peak voltage, sliding enhances current stability, single-electrode simplifies device integration, and freestanding layers enable bidirectional harvesting (Jayachandrababu, 2017; Slater & Tan, 2024).

Material selection critically governs TENG performance. Conventional polymers such as polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE) occupy

opposite ends of the triboelectric series, yet embedding nanomaterials including graphene, carbon nanotubes, or metal–organic frameworks (MOFs) can enhance dielectric constant and surface roughness, yielding power-density improvements exceeding 200 % (Zhang & Ölin, 2020; Rahman et al., 2023). I

From the MOFs, zeolitic imidazolate frameworks (ZIFs) have been particularly transformative: halogenated linkers in ZIF-8 allow precise control of charge polarity and retention, boosting output by 25 % under humid conditions (Noman et al., 2024), while woody-templated ZIF-67 structures have achieved record peak power densities of 2.3 W/m² in flexible TENGs (Gao et al., 2024). Facile, scalable syntheses such as stovetop pressure-cook deposition of ZIF-67 onto textiles enable uniform MOF coatings without harsh solvents, paving the way for low-cost, large-area wearable modules (Dhal et al., 2024) and roll-to-roll manufacturing of MOF-303 films for meter-scale production (Velpula et al., 2024).

In addition, hybrid composites further broaden application scope: hydrogel–MOF TENGs deliver outstanding stretchability and biocompatibility for biomotion sensing (Rahman et al., 2023); 2D-nanomaterial/MOF hybrids synergize interfacial charge transfer (Liu, Ping, & Ying, 2021); MOF/COF grafts yield mechanically robust, high-output generators (Shao et al., 2023); and waste-valorized, spent-catalyst Mo-MOF TENGs exemplify sustainable design (Swain et al., 2023). End-group-tunable MOF/polymer composites demonstrate superior environmental stability (More et al., 2022), while electrohydrodynamic printing of ZIF-67 arrays achieves spatially resolved energy harvesting for flexible electronics (Memon et al., 2024). Chlorinated ZIF ligands improve surface adhesion and charge retention under humid conditions (Ye & Tan, 2023), and foundational insights into intergrown zeolite-beta polymorphs guide the design of next-generation frameworks with optimized channel connectivity for charge transport (Yu et al., 2012). Together, these advances position TENGs as a versatile, scalable platform for autonomous, maintenance-free energy harvesting in the era of ubiquitous electronics.

2.1.1 Historical Development and State of the-Art TENG Technologies

The concept of harvesting ambient mechanical energy via contact electrification can be traced back centuries, but it was not until the early 2010s that nanoscale engineering enabled practical devices. In 2012, Fan, Tian, and Wang first demonstrated a vertical contact–separation TENG using PTFE and nylon films, achieving open-circuit voltages above 1 kV and power densities exceeding 50 mW/cm² under optimized contact pressure (Pu et al., 2017; Zhao, Lin, Li, & Wang, 2021). This breakthrough spurred intensive theoretical work: Niu, Wang, Lin, and Zi (2014) developed a comprehensive sliding-mode model, showing that micro- and nano-textured surfaces, combined with precise gap control, could maximize surface charge density and guide the design of four fundamental operation modes including vertical contact–separation, lateral sliding, single-electrode, and freestanding triboelectric-layer (Niu et al., 2014; Slater & Tan, 2024).

Early devices used simple polymer pairings (e.g., PDMS vs. PTFE) to span the triboelectric series, but performance was limited by low dielectric constants and smooth surfaces (Dharmasena, Jayawardena, & Silva, 2017). The integration of graphene nanosheets into PDMS matrices introduced hierarchical roughness and boosted dielectric permittivity, resulting in over twofold increases in charge output (Kim, Lee, Kim, & Jeong, 2021). Zhang and Ölin (2020) extended this approach by embedding MOF nanoparticles within polymer films, achieving a 40 % rise in effective dielectric constant and a threefold enhancement in power density. Concurrently, theoretical studies highlighted how such nanocomposites could overcome the trade-off between mechanical flexibility and electrical output (Zhang & Ölin, 2020; Dharmasena et al., 2017).

Between 2018 and 2020, efforts shifted towards novel framework materials. Hydrogel–MOF hybrids enabled stretchable, biocompatible TENGs suitable for direct skin integration, with sustained output over 10,000 deformation cycles (Rahman et al., 2023). Zeolitic imidazolate frameworks (ZIFs) emerged as particularly promising:

Noman et al. (2024) demonstrated halogenated ZIF-8 linkers that tuned triboelectric polarity and charge retention, boosting output by 25 % under 90 % relative humidity. Gao et al. (2024) employed woody cellulose templates to grow ZIF-67 “biphase blocking” structures, achieving record peak power densities of 2.3 W/m² in flexible mode. These bio-templated devices not only improved performance but also highlighted sustainable, low-impact fabrication routes (Gao et al., 2024; Rahman et al., 2023).

Scalability became a focus as TENGs moved toward real-world applications. Dhal et al. (2024) introduced a stovetop pressure-cook synthesis of ZIF-67 directly onto textile fibers, eliminating harsh solvents and high-temperature reactors while ensuring uniform MOF coverage. Velpula et al. (2024) demonstrated roll-to-roll production of MOF-303 films, enabling meter-scale device manufacturing with consistent output. Electrohydrodynamic ink-jet printing by Memon et al. (2024) further allowed spatial patterning of ZIF-67 arrays on flexible substrates, achieving localized energy harvesting densities suitable for smart skin applications. Parallel efforts by Swain et al. (2023) repurposed spent-catalyst Mo-MOFs for eco-friendly TENGs, combining waste valorization with energy harvesting (Dhal et al., 2024; Velpula et al., 2024; Memon et al., 2024; Swain et al., 2023).

By 2021, the community had converged on hybrid architectures that integrate multiple functional materials. More et al. (2022) developed end-group-tunable MOF/polymer composites that retained 90 % of their initial output after 1,000 hours at 85 °C/85 % RH, addressing long-term stability challenges. Liu, Ping, and Ying (2021) reviewed 2D-nanomaterial/MOF hybrids, emphasizing synergistic enhancements in interfacial charge transfer. Rana et al. (2024) expanded on these findings, demonstrating fully self-powered active sensing platforms that combined MOF-reinforced TENGs with integrated signal processing. Work by Jayachandrababu (2017) on multi-mode devices underscored the importance of mechanical design in achieving both high output and durability, paving the way for wearable robotics and autonomous sensor networks (Jayachandrababu, 2017; More et al., 2022; Liu, Ping, & Ying, 2021; Rana et al., 2024).

Today, TENGs represent a mature, versatile technology platform. From initial lab-scale PTFE/nylon stack generators to roll-to-roll-produced MOF composites and printed ZIF arrays, the field has addressed key challenges in output, durability, and manufacturability. As the IoT ecosystem nears 200 billion connected sensors, these advances position TENGs to fulfill the critical need for maintenance-free, autonomous power sources (Rana et al., 2024; Velpula et al., 2024), marking a new era in sustainable energy harvesting.

2.1.2 Fundamentals of Triboelectricity And Its Mechanisms

The underlying mechanism of TENGs, the triboelectric effect referred to as triboelectric charging involves materials becoming electrically charged when they come into contact and are subsequently separated (Niu, Wang, Lin, & Zi, 2014; Zhang & Ölin, 2020). This phenomenon, driven by friction between two dissimilar surfaces, generates electricity and is termed triboelectricity (Fan, Tian, & Wang, 2012; Dharmasena, Jayawardena, & Silva, 2017). This effect is a common source of static electricity in everyday life, with the charge polarity and intensity depending on the specific materials involved (Zi, Lin, & Wang, 2016; More et al., 2022; He et al., 2018). The triboelectric effect is primarily governed by two mechanisms: contact electrification, where electric charge transfers between materials in contact, and electrostatic induction, where an external electric field redistributes charges within a material (Niu et al., 2014; Fan et al., 2012; Wang, Chen, & Lin, 2014). While tribology (the study of friction and wear between surfaces) and flexoelectricity (the generation of electric charge due to mechanical strain) may also influence triboelectric phenomena, the primary contributors remain contact electrification and electrostatic induction (Slater & Tan, 2024; Zhang et al., 2014; Zi et al., 2016). TENGs thus offer a simple, sustainable, and highly effective approach to energy harvesting, with broad potential applications in renewable energy, active sensing, and nanosystem technologies (Xu et al., 2017; Pu et al., 2017; Rahman et al., 2023).

The process of generating electricity through adhesion is referred to as the triboelectric effect or triboelectric charging (Fan et al., 2012; Niu et al., 2014; Wang, Lin, & Wang, 2013). This phenomenon occurs through contact electrification, where one material

becomes electrically charged after separating from another material it was in contact with (Slater & Tan, 2024; Zhang & Ölin, 2020; Gao et al., 2024). When two different materials come into contact, electrons transfer between them due to friction, equalizing the electrical potential (Zi et al., 2016; Xu et al., 2017; Pu et al., 2017). Upon separation, the materials may carry opposite charges—one positively and the other negatively charged. When these charged surfaces interact with an oppositely charged surface, an electric discharge can occur (He et al., 2018; Noman et al., 2024; Zhu et al., 2019). Triboelectricity involves generating electricity when two distinct materials collide or rub against each other, leading to a significant flow of electrons between them while maintaining a potential difference (Liu, Ping, & Ying, 2021; Kim et al., 2021; Pu et al., 2020). For example, rubbing a plastic comb through hair generates static electricity, a common everyday experience of the triboelectric effect (Wang, Chen, & Lin, 2014; Cheng et al., 2020; Park et al., 2019). The charge's polarity and strength depend on factors such as material type, strain, temperature, and surface roughness (Rana et al., 2024; Jeong et al., 2020; Rahman et al., 2023). This effect laid the groundwork for the development of the triboelectric nanogenerator (TENG) in 2012 at the Georgia Institute of Technology (Fan et al., 2012; Niu et al., 2014; Dharmasena et al., 2017).

Triboelectricity, primarily driven by electron transfer between materials, creates high voltage when the surfaces separate, initiating electron flow (Zhao, Lin, Li, & Wang, 2021; Gao et al., 2024; Guo & Wang, 2020). The first TENG, developed in 2012, used Kapton and polyester in a contact-separation mode (Wang, Lin, & Wang, 2013; Fan et al., 2012; Niu et al., 2014). Other modes, including lateral sliding, single-electrode, and freestanding triboelectric layered modes, were introduced in subsequent research (Yang, Cheng, & Wang, 2022; Zhang & Ölin, 2020; Wang, Chen, & Lin, 2014). These modes optimize the triboelectric charge density based on the contact force and design, with larger contact areas and stronger forces enhancing output performance (Zi et al., 2016; Xu et al., 2017; Pu et al., 2017).

TENGs are highly versatile and compact devices that harvest mechanical energy and convert it directly into electrical energy without requiring additional converters or transducers (Guo et al., 2018; He et al., 2018; Han et al., 2018). They can be applied

to various fields, such as self-powered sensors, including motion, acceleration, acoustic, chemical, and photoelectric sensors (Yao, Wang, & Pu, 2019; Zhu et al., 2019; Liu et al., 2021). With a power output ranging from 0.1 to 100 mW/cm², optimizing materials and design parameters is critical for maximizing their efficiency (Li et al., 2020; Pu et al., 2020; Wang et al., 2018). Strong triboelectric materials with low permittivity substrates beneath the contact layer are essential for improving performance (Cheng et al., 2020; Park et al., 2019; More et al., 2022).

The triboelectric effect can be observed in everyday life, such as rubbing a balloon against hair, causing the hair to stand up due to opposite charges (Jeong et al., 2020; Huang et al., 2021; Cao et al., 2021). Similarly, a charged balloon can bend a thin stream of water, as the water molecules are attracted to the charged surface (Tao, Cheng, & Wang, 2022; Zhang & Wang, 2022; Zhao et al., 2021). These simple demonstrations highlight the principle behind TENGs, which harness the triboelectric effect to generate electricity.

Over the last decade, researchers have advanced the design and functionality of TENGs to power electronic devices, sensors, and potentially larger-scale applications (Gao et al., 2024; Guo & Wang, 2020; Xu et al., 2017). Through innovative designs and operating modes, TENGs continue to evolve as an efficient, eco-friendly solution for harvesting ambient mechanical energy (Pu et al., 2017; He et al., 2018; Han et al., 2018).

2.2 Theory of the TENG, Working Principles and Modes

Triboelectric nanogenerators (TENGs) represent an emerging technology capable of harvesting mechanical energy from ambient environments through the coupling of contact electrification and electrostatic induction. The operational principle of a TENG is fundamentally rooted in the triboelectric effect, where two materials with different electron affinities come into contact and subsequently separate, inducing surface charge transfer. As the surfaces separate, an electrostatic potential difference develops, driving a current through the external circuit to balance the generated charges. This

dynamic process can be mathematically described by the time-dependent current Equation 2.1:

$$i(t) = \frac{dQ(t)}{dt} = C(t) \frac{dV(t)}{dt} + V(t) \frac{dC(t)}{dt} \quad (2.1)$$

where $C(t)$ represents the time-varying capacitance, and $V(t)$ is the instantaneous potential difference across the electrodes (Zhang et al., 2024).

One of the most critical parameters that directly affects the output performance of triboelectric nanogenerators (TENGs) is the displacement current. In TENGs, the displacement current differs from the standard expression given in Maxwell's equations. In classical theory, the electric displacement vector D is described as given Equation (2.2).

$$\begin{aligned} D &= \epsilon_0 E + P \\ D_{teng} &= \epsilon_0 E + P + P_s \end{aligned} \quad (2.2)$$

where E is the external electric field, and P is the polarization vector induced by the field. However, in TENGs, the surface charges are not induced by an external electric field, but instead result from direct contact between materials with differing electron affinities. Therefore, an additional term P_s must be included in the displacement field to account for charge generation due to contact electrification (Niu, Wang, Lin, & Zi, 2014; Dharmasena, Jayawardena, & Silva, 2017). P_s represents the influence of electrostatic charges on surfaces or within the bulk material and is dependent on the change rate of the system's boundary shape. The total displacement current density J_D in a TENG can be expressed as Equation (2.3).

$$J_D = \frac{\partial D}{\partial t} + \frac{\partial P_s}{\partial t} = \epsilon \frac{\partial E}{\partial t} + \frac{\partial P_s}{\partial t} \quad (2.3)$$

The output current I of a TENG with surface area A can be further estimated using the following Equation (2.4).

$$I \approx A\sigma_T \left(\frac{dH}{dT} \right) \left(\frac{d_1 \varepsilon_0 / \varepsilon_1 + d_2 \varepsilon_0 / \varepsilon_2}{d_1 \varepsilon_0 / \varepsilon_1 + d_2 \varepsilon_0 / \varepsilon_2 + z^2} \right) \quad (2.4)$$

where σ is the triboelectric surface charge density, v is the mechanical excitation speed, d_1 and d_2 are the thicknesses of the triboelectric layers, ε_1 and ε_2 are their respective dielectric constants, and z is the interlayer gap (Zhou et al., 2021; Zhang et al., 2018). The dielectric properties are determined by material chemistry, while surface charge density is influenced by material type, morphology, and contact efficiency (Fan et al., 2012).

To maximize performance, TENGs should be configured in operational modes that match the mechanical energy source. The three most common working modes are contact-separation, lateral sliding, and freestanding triboelectric layer modes (Niu, Wang, Lin, & Zi, 2014; Slater & Tan, 2024). Each mode may be implemented in either a single-electrode or dual-electrode configuration. The contact-separation mode is the most straightforward. In this configuration, two different dielectric materials are positioned face-to-face, each backed with a conductive electrode. When contact occurs, charges transfer between the surfaces; upon separation, a potential difference drives current through the external circuit (Jayachandrababu, 2017). Repeating the contact and separation generates alternating current (AC), which can be rectified into direct current (DC) using suitable circuitry (Zhang & Ölin, 2020).

Among various material systems employed in TENGs, metal-organic frameworks (MOFs), particularly zeolitic imidazolate frameworks (ZIFs), have gained significant attention due to their unique structural and electronic properties. ZIFs such as ZIF-8 and ZIF-67 consist of metal ions (e.g., Zn^{2+} or Co^{2+}) coordinated with imidazolate linkers, forming highly porous, crystalline networks with exceptionally high specific surface areas and tunable porosity. The surface functional groups and large interface

area offered by these materials contribute directly to enhancing triboelectric charge density (σ) by increasing the density of active charge transfer sites.

The surface charge generation during contact electrification can be modeled by an adapted Johnson-type Equation (2.5).

$$\sigma = eN_s (\alpha_{contact} - \alpha_{substrate}) \quad (2.5)$$

where e denotes the elementary charge, N_s is the surface density of active sites, and α refers to the material-dependent electron affinity (Zhang & Ölin, 2020; Noman et al., 2024). MOF-ZIF structures increase N_s significantly due to their ultrahigh surface area, thereby promoting enhanced charge accumulation compared to conventional polymer or metal-based tribo-pairs.

One of the primary advantages of incorporating ZIF nanoparticles into the triboelectric layers is the effective enhancement of the surface area (A_{eff}). This enhancement directly influences the overall charge generation, as the total charge (Q) is proportional to $\sigma \times A_{eff}$. In practical systems, the inclusion of ZIF-8 in polymer matrices such as PDMS or PVDF has demonstrated a near doubling of electrical output due to increased interfacial charge storage (Khandelwal, Chandrasekhar, Maria Joseph Raj, & Kim, 2019; More et al., 2022). Additionally, the intrinsic microporosity of ZIF structures facilitates electron trapping within the pores, contributing to prolonged charge retention and improved power output stability (Velpula et al., 2024; Slater & Tan, 2024).

The electron transfer mechanisms at the MOF-metal interface involve complex interfacial physics. Recent studies suggest that beyond classical contact electrification, quantum band-bending and flexoelectricity significantly affect charge transfer dynamics. At the nanoscale, local deformation of ZIF frameworks upon contact can induce flexoelectric polarization, creating internal electric fields that modulate electron tunneling across the interface. This process can be mathematically modeled using a modified thermionic emission Equation (2.6)

$$J = J_0 e^{-(\phi - eE_{flex}d)/k_B T} \quad (2.6)$$

where J is the current density, J_0 the pre-exponential factor, Φ the interfacial barrier height, E_{flex} the flexoelectric field strength, d the effective tunneling distance, and $k_B T$ the thermal energy (Dharmasena, Jayawardena, & Silva, 2017; Slater & Tan, 2024). The structural flexibility of ZIF crystals allows for the generation of substantial E_{flex} fields under mechanical strain, thereby facilitating efficient charge transfer.

The capacitance variation as a function of separation distance further elucidates the TENG behavior in MOF-ZIF-based systems. The capacitance at any instant can be expressed as Equation (2.7).

$$C(t) = \frac{\epsilon_0 \epsilon_r A_{eff}}{x(t)} \quad (2.7)$$

where ϵ_0 is the vacuum permittivity, ϵ_r the relative permittivity of the dielectric material, A_{eff} the effective contact area, and $x(t)$ the separation distance between tribo-layers. Correspondingly, the open-circuit voltage ($V(t)$) is given in Equation (2.8).

$$V(t) = \frac{\sigma x(t)}{\epsilon_0 \epsilon_r} \quad (2.8)$$

Equation (2.8) indicates that larger charge density and separation distance yield higher output voltages.

These experimental data across various MOF-ZIF TENG systems support these theoretical predictions. For instance, Barsiwal et al. (2022) demonstrated that ZIF-67/PMMA composites achieved output voltages of approximately 300 V and short-circuit currents of 47.5 μ A, yielding a power density of 593 mW/m². Gao et al. (2024) reported a record power density of 2.3 W/m² using a woody-templated ZIF-67

“biphase blocking” structure on cellulose fibers. Babu et al. (2023) achieved long-term operational stability over 40 000 continuous cycles without significant performance degradation by direct-growth of ZIF-67 on flexible substrates. This superior durability arises from the intrinsic mechanical robustness of ZIF crystals, which can exhibit bulk moduli on the order of gigapascals, as evidenced by computational and experimental studies on ZIF framework mechanics.

2.2.1 Explanation of Contact-Separation, Sliding, and Freestanding Layer Modes

Triboelectric nanogenerators (TENGs) can operate under various mechanical coupling configurations, which dictate their energy harvesting capabilities, structural design, and suitability for different practical applications. Understanding these working modes is fundamental for the rational design of advanced TENG architectures, especially when integrating MOF-ZIF nanomaterials to enhance triboelectric performance (Fan et al., 2012; Zi et al., 2015).

When two dissimilar materials are brought into contact under external pressure, physical contact enables direct interaction between their surface atomic layers shown in Figure 2.1. Due to differences in electron affinities (or work functions), one material tends to donate electrons while the other accepts them, resulting in net charge transfer. This charge exchange process is governed by the triboelectric series and can involve several sub-mechanisms such as electron cloud overlap, ion transfer, and material bond polari...

The net surface charge density σ generated upon contact can be approximated by Equation (2.9)

$$\sigma = eN_s(\Delta\chi) \quad (2.9)$$

where e is the elementary charge, N_s is the number of active surface sites per unit area, and $\Delta\chi$ is the difference in surface electronegativity or electron affinity. MOF-ZIF

structures enhance N_s substantially due to their highly porous architectures (Liu et al., 2023; Barsiwal et al., 2022; Noman et al., 2024).

Upon removal of the applied pressure, the two surfaces separate from each other. Since the surfaces are now oppositely charged but spatially separated, a significant electric field is established in the gap between them. The electrostatic field E generated across the separation gap $x(t)$ can be described as Equation (2.10)

$$E(t) = \frac{\sigma}{\epsilon_0 \epsilon_r} \quad (2.10)$$

where ϵ_0 is vacuum permittivity and ϵ_r is the relative permittivity of the gap medium. The open-circuit voltage VOC between the electrodes increases linearly with separation distance as Equation (2.11)

$$V_{oc} = \frac{(\sigma \cdot x(t))}{\epsilon_0 \epsilon_r} \quad (2.11)$$

Thus, a greater separation leads to a larger potential difference, which drives subsequent current flow. MOF-ZIF-based surfaces are advantageous here because their microstructured surface topography allows highly elastic deformation, which promotes more complete contact during compression and a wider effective separation range during release (Huang et al., 2021; Velpula et al., 2024).

As the separation between the tribo-surfaces increases, the induced potential difference drives electrons through the external circuit. This current flow attempts to neutralize the unbalanced electrostatic field established by the charge separation.

In MOF-ZIF systems, the presence of nanoscopic pores and flexible lattice structures enhances both effective area A and charge-trapping ability, which leads to more sustained and higher output currents. Moreover, the porous ZIF layers can delay charge

recombination, extending the discharge time and improving energy-harvesting efficiency (Potu et al., 2023; Dhal et al., 2024).

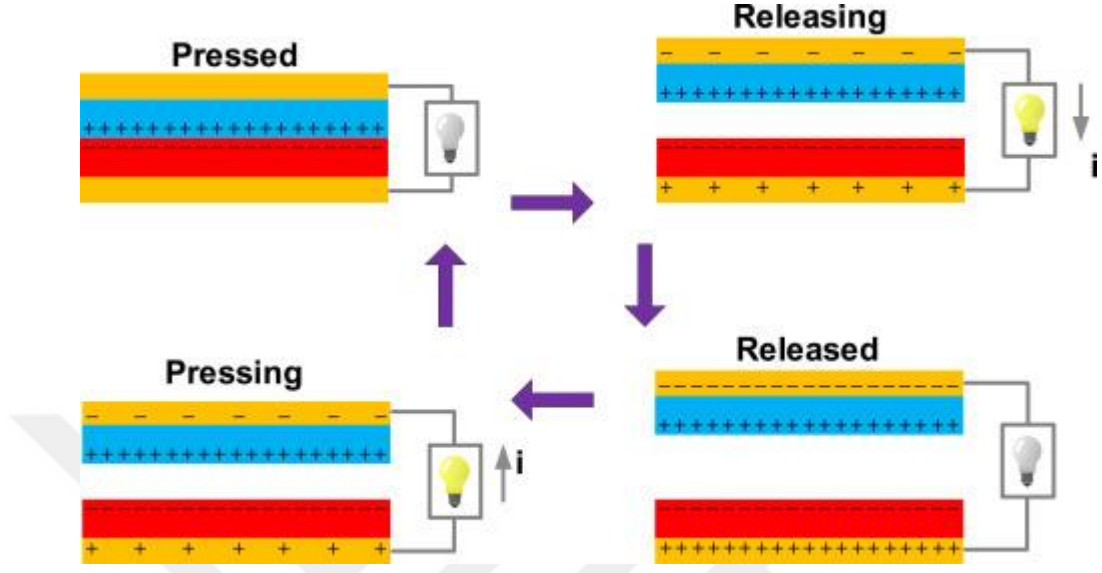


Figure 2. 1: Working Principle of a Triboelectric Nanogenerator in the Contact–Separation (Pressing–Releasing) Cycle (Lin et al., 2012).

Triboelectric nanogenerators operating in the lateral sliding mode given in Figure 2.2 harvest mechanical energy through relative in-plane displacement between two dielectric surfaces. Unlike the vertical contact-separation mode, this configuration involves continuous lateral motion while maintaining partial contact between the surfaces. The energy harvesting mechanism in this mode can be explained through three sequential physical reflexes: interfacial charge generation, dynamic charge redistribution, and induced current flow.

As the two surfaces initially contact, electron transfer occurs at localized contact regions due to differences in electron affinity and surface work functions. However, due to lateral motion, new microscopic contact sites are continuously generated and broken. This results in distributed charge transfer along the sliding interface. The instantaneous local charge density σ can be expressed as Equation (2.9).

As lateral sliding progresses, previously charged contact areas are separated while fresh contact zones are continuously created. The relative displacement dynamically redistributes surface charges across the interface. This displacement-controlled charge

separation generates spatial charge gradients that induce potential differences across electrodes. The output current is determined by Equation (2.12).

$$V(t) = \frac{\sigma x(t)}{\epsilon_0 \epsilon_r} \quad (2.12)$$

Here, the change in overlapping area $A(t)$ is directly proportional to the sliding velocity. Faster sliding speeds induce larger instantaneous currents. MOF-ZIF materials increase $A(t)$ via micro-contact asperities and stabilize charge retention.

The time-varying potential difference caused by dynamic charge separation drives electrons through the external load. As the overlapping area changes, the spatial separation of localized charges maintains a continuous flow of current. The induced voltage during sliding can be expressed as Equation (2.13)

$$V_{oc} = \frac{(\sigma \cdot \Delta x(t))}{\epsilon_0 \epsilon_r} \quad (2.13)$$

where $\Delta x(t)$ is the relative lateral displacement, ϵ_0 is vacuum permittivity, and ϵ_r is relative permittivity of the dielectric. MOF-ZIF-modified tribo-surfaces further stabilize this induced voltage by extending charge retention time and improving energy conversion efficiency.

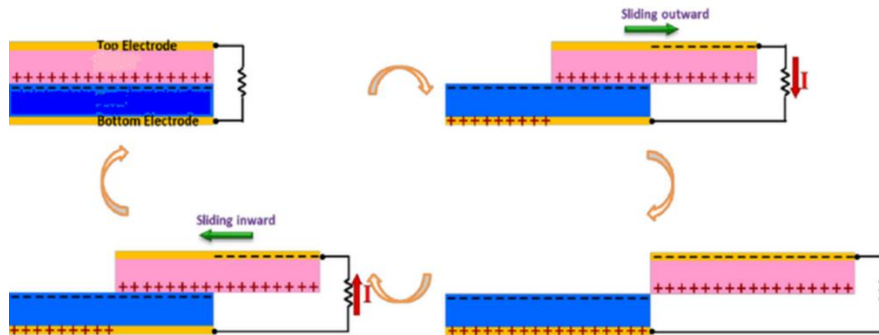


Figure 2.2: Operational cycle of a sliding-contact triboelectric nanogenerator showing charge transfer and current generation (Wang, Lin, & Wang, 2015).

The single-electrode mode of triboelectric nanogenerators (TENGs) given in Figure 2.3 represents one of the most versatile and structurally simplified configurations within the triboelectric family. In this mode, only one of the triboelectric layers is electrically connected to an electrode, while the counter material remains electrically floating or interacts directly with the ambient environment, effectively functioning as a virtual ground. This configuration enables broad adaptability, making it highly attractive for flexible, wearable, and non-contact sensing systems (Niu et al., 2013; Choi et al., 2023; Jeong et al., 2020; Hinchet et al., 2018; Xu et al., 2017).

The fundamental mechanism of the single-electrode mode is governed by the interplay between contact electrification and electrostatic induction. Initially, when the triboelectric layer physically contacts a counter surface, be it a solid material, fluid interface, or biological surface, charge exchange occurs at the molecular level. This charge transfer is predominantly driven by differences in surface electron affinity or chemical potential between the two contacting materials. The net surface charge density σ generated during this process can be theoretically described by Equation (2.9).

Following contact, the surfaces undergo separation under external mechanical stimuli, leading to spatial displacement of oppositely charged surfaces. As the separation distance $x(t)$ varies temporally, a macroscopic dipole moment is established between the charged dielectric and the environment. This varying dipole moment leads to dynamic changes in the electrostatic field and consequently induces a time-dependent potential difference between the single electrode and the reference ground. The instantaneous open-circuit voltage $V_{oc}(t)$ generated can be modeled as Equation (2.12). The single-electrode system can be analogized as a dynamic variable capacitor with its capacitance expressed by Equation (2.7). The transient current $I(t)$, which flows through the external circuit in response to the dynamic potential change, can be mathematically expressed as Equation (2.14)

$$I(t) = \frac{dQ(t)}{dt} = \sigma I(t) = \frac{dx(t)}{dt} \frac{1}{\epsilon_0 \epsilon_r} \quad (2.14)$$

In the context of material optimization, incorporation of metal-organic frameworks (MOFs), particularly zeolitic imidazolate frameworks (ZIFs), into the triboelectric layers has emerged as a transformative approach to significantly enhance device performance (Liu et al., 2023; Barsiwal et al., 2022; Rahman et al., 2022; Noman et al., 2024). The nanostructured morphology and intrinsic porosity of ZIF-based materials contribute to multiple synergistic benefits. Firstly, the exceptionally high specific surface area of MOF-ZIF frameworks elevates the density of active charge transfer sites (N_s), thereby increasing the overall triboelectric charge density. Secondly, the porous nanocavities serve as effective charge trapping centers, mitigating rapid charge recombination and extending the charge retention time, which is critically important for stable and sustained current generation. Thirdly, the inherent dielectric properties of MOFs modulate the relative permittivity ϵ_r , amplifying the capacitance variations during dynamic operation and consequently enhancing the induced potential difference.

Moreover, MOF-ZIF integration offers substantial operational stability in humid or chemically aggressive environments due to the excellent chemical stability and hydrophobic characteristics of certain ZIF frameworks. This environmental robustness is particularly advantageous for wearable and biomedical applications, where external fluctuations in humidity and chemical exposure are frequent and can otherwise degrade triboelectric performance (Sun et al., 2023; Gao et al., 2024; Tao et al., 2022).

The overall power output $P(t)$ of the single-electrode TENG can be expressed as Equation (2.15).

$$P(t) = \frac{V(t)^2}{R} \quad (2.15)$$

In conclusion, the single-electrode mode of TENGs given in Figure 2.3, while structurally simple, embodies complex interfacial charge dynamics governed by both material chemistry and electrostatic physics. The strategic incorporation of MOF-ZIF nanomaterials provides a highly effective pathway for performance enhancement,

enabling the development of next-generation self-powered devices capable of operating reliably across diverse and dynamic environmental conditions.

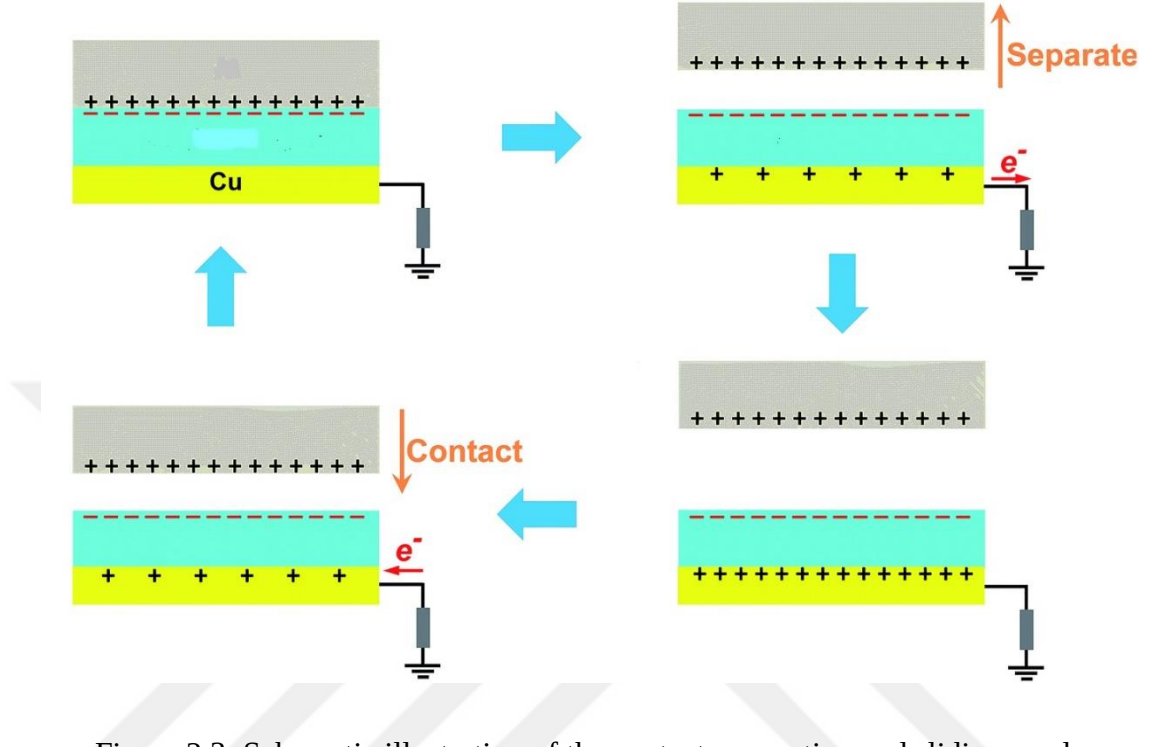


Figure 2.3: Schematic illustration of the contact–separation and sliding-mode working cycle of a Cu-based triboelectric nanogenerator (Niu et al., 2015).

The freestanding triboelectric-layer mode represents one of the most distinctive and high-performance configurations within the triboelectric nanogenerator (TENG) family. Unlike vertical contact-separation or lateral sliding modes, the freestanding mode employs an electrically floating triboelectric layer that moves independently between two stationary electrodes. As the freestanding dielectric layer oscillates or moves under mechanical stimuli, charge redistribution occurs between the fixed electrodes.

The fundamental working principle of the freestanding mode given in Figure (2.4) is rooted in the dynamic redistribution of surface charges via electrostatic induction. Initially, contact electrification occurs between the freestanding layer and both stationary electrodes during initial contact. This charge transfer is governed by differences in work function or electron affinity between the materials. The net charge density σ generated can be represented by Equation (2.9)

Upon subsequent lateral or vertical motion of the freestanding layer, asymmetry is introduced in the spatial distribution of charges with respect to the two electrodes, resulting in a varying electrostatic potential difference across the electrodes. The instantaneous transferred charge $Q(t)$ can be expressed by Equation (2.16)

$$Q(t) = \sigma A \frac{x(t)}{d + x(t)} \quad (2.16)$$

where A is the effective contact area, d is the separation distance between the stationary electrodes, and $x(t)$ is the displacement of the freestanding layer relative to the electrodes (Niu et al., 2015). The induced open-circuit voltage $VOC(t)$ is directly proportional to the displacement as given in Equation (2.13)

The freestanding mode exhibits high-frequency energy harvesting capabilities, especially suitable for oscillatory, vibrational, and rotational motions in ambient environments (Han et al., 2018; Luo et al., 2021).

Material engineering has enabled significant performance enhancement through the incorporation of metal-organic frameworks (MOFs), particularly zeolitic imidazolate frameworks (ZIFs), into the freestanding triboelectric layers. The porous microstructure and high surface area of MOF-ZIF composites provide numerous advantages. Firstly, the increased number of active charge transfer sites boosts the initial charge density σ (Khandelwal et al., 2019; Zhang & Olin, 2020; Priya & Inman, 2009). Secondly, the nanoporous morphology enables enhanced charge trapping.

Furthermore, MOF-ZIF structures exhibit excellent mechanical flexibility and fatigue resistance, ensuring operational stability over millions of working cycles even under high-frequency oscillations. The flexible lattice of ZIF frameworks also contributes to additional flexoelectric effects, wherein bending-induced polarization further enhances localized charge density and current output during dynamic deformation (Chen et al., 2016; Zhu et al., 2019).

In summary, the freestanding triboelectric-layer mode offers superior mechanical adaptability and high energy conversion efficiency through independent charge redistribution mechanisms. The integration of MOF-ZIF nanostructures plays a critical role in maximizing the triboelectric charge generation, charge retention, and long-term durability, enabling advanced applications in environmental vibration harvesting, smart infrastructure monitoring, and wearable power systems.

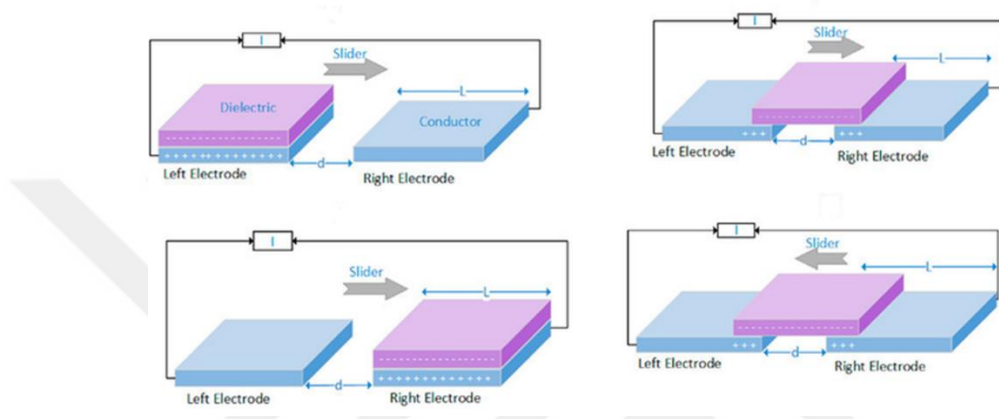


Figure 2.4: Four-stage schematic of the sliding-mode operation of a triboelectric nanogenerator, showing the relative motion of the dielectric slider between left and right electrodes and the corresponding charge transfer cycle (Wang et al., 2013).

2.2.2 Comparative analysis of TENG Modes

A systematic comparative analysis of these modes given in Table 2.1 provides crucial insight for the rational selection and optimization of TENG configurations, guiding the tailoring of materials, device architectures, and operational protocols to maximize key performance metrics such as open-circuit voltage, short-circuit current and power density while also enhancing long-term stability. Such mode-specific design rules enable the development of application-driven TENGs, from ultra-compact, low-frequency wearable sensors to high-throughput, large-area energy harvesters. The vertical contact-separation mode represents the most fundamental and widely studied configuration of TENGs. In this mode, two dielectric surfaces are brought into periodic normal contact under external mechanical force, allowing triboelectric charge transfer via surface contact and subsequent separation (Fan et al., 2012; Wang et al.,

2017; Wang, S., Lin, & Wang, 2012; Wang, Z. L., 2014; Wang, Chen, & Lin, 2015). The energy conversion process primarily relies on the magnitude of contact-induced surface charge density (σ), separation distance ($x(t)$), and relative permittivity. The lateral sliding mode involves the continuous tangential displacement of triboelectric surfaces while maintaining partial contact (Lin et al., 2014; Dharmasena et al., 2017; Park et al., 2019). New contact regions are constantly formed and separated, enhancing charge-transfer frequency and generating stable output under continuous motion.

This configuration is highly effective for rotational energy harvesting, textile-based wearable electronics, and mechanized systems featuring cyclical sliding motions. By tailoring the interfacial geometry and sliding stroke, one can optimize both the charge transfer rate and the instantaneous power density, making sliding-mode TENGs particularly attractive for applications requiring continuous, high-frequency electrical output. Nevertheless, interface abrasion and precise alignment control remain critical challenges that must be addressed to ensure long-term durability and reliable performance.

Although single-electrode TENGs achieve high design flexibility and exceptional compatibility with wearable and biomedical devices, their energy output is often constrained by parasitic capacitance to ground and environmental noise. The lack of a dedicated counter-electrode return path can limit charge induction efficiency and lower the signal-to-noise ratio. To overcome these drawbacks, recent studies have explored patterned dielectric surfaces to increase effective contact area, optimized electrode geometries to enhance local electric fields, and bespoke impedance-matching circuits to maximize power transfer (Niu et al., 2015; Wang & Wang, 2019; Dudem et al., 2018; Yao et al., 2019; Potu et al., 2023; Li et al., 2023). Such innovations have substantially improved both the peak power density and baseline stability of single-electrode TENGs in real-world applications.

The freestanding triboelectric-layer mode employs an isolated dielectric sheet that oscillates between two symmetrically placed stationary electrodes, inducing alternating current without direct physical contact (Wang et al., 2014; Park et al., 2019; Wang et al., 2022). This configuration excels at high-frequency harvesting from

vibrations, wind, and rotational motions while maintaining excellent durability due to minimal solid–solid wear. Precise mechanical alignment and controlled suspension of the moving layer are critical; accordingly, recent work has introduced microstructured surface patterning to amplify interfacial electric fields, magnetic or air-bearing levitation to reduce friction, and multilayer dielectric stacks to extend the operational bandwidth. These advances have propelled freestanding-mode TENGs toward reliable, high-throughput energy harvesters for next-generation self-powered systems

Table 2.1: Comparative Summary Table

Mode	Charge Transfer Mechanism	Output Efficiency	Wear Resistance	Structural Complexity	Key Applications
Contact-Separation	Normal contact	High (instantaneous)	Low (fatigue issue)	Moderate	Impact energy, footfalls, pulse sensors
Lateral Sliding	Tangential contact	Moderate to high	Moderate	Higher	Rotary machines, wearables
Single-Electrode	Ground-based coupling	Low to moderate	High	Low (simplified)	Wearables, biomedical sensing
Freestanding Layer	Induction via displacement	High (continuous)	Very high	Higher	Vibrations, wind, oscillations

The selection of appropriate TENG mode heavily depends on targeted application demands. For instance, vertical contact-separation mode is highly suitable for biomechanical energy harvesting from human motion due to its high instantaneous output per cycle (Wang et al., 2017; Cheng et al., 2020; Liu et al., 2020; Cao et al., 2021). Lateral sliding mode excels in continuous mechanical systems such as rotating wheels or conveyor belts (Lin et al., 2014). Single-electrode mode offers excellent potential for wearable electronics, flexible biosensors.

While each TENG working mode offers distinct advantages, the optimal choice depends on a balanced consideration of mechanical operation conditions, desired power output, material durability, device complexity, and environmental exposure. The continuous advancement in material engineering, particularly the integration of MOF-ZIF frameworks, offers synergistic improvements across multiple modes, expanding the practical application horizon for TENG technologies in self-powered sensing, biomedical monitoring.

2.3 Materials in TENGs

The selection of materials is one of the most crucial factors in determining the efficiency, stability, and application range of triboelectric nanogenerators (TENGs). As triboelectric energy conversion fundamentally relies on charge transfer between materials with different electron affinities, careful engineering of surface chemistry, morphology, and dielectric properties of the contacting materials can dramatically influence device performance. In recent years, advances in material science have enabled the design of highly efficient, durable, and multifunctional TENG devices, allowing their application to expand into numerous technological fields such as wearables, biomedical devices, environmental monitoring, and large-scale energy harvesting systems (Wang et al., 2017; Niu et al., 2015; Pu et al., 2017; Cao et al., 2021; Liu et al., 2020; Wang et al., 2024).

In general, the materials used in TENGs can be categorized into two broad classes: tribo-positive materials and tribo-negative materials, according to their tendency to donate or accept electrons upon contact. Tribo-positive materials: These materials exhibit a higher tendency to lose electrons during contact electrification. Common examples include polymers such as nylon, silk, wool, and polyamide (Dharmasena et al., 2017). Tribo-negative materials: These materials tend to attract electrons and become negatively charged. Polymers like polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), and fluorinated ethylene propylene (FEP) belong to this category (Dudem et al., 2018).

The difference in electron affinity between paired materials largely governs the triboelectric charge density, with larger differences typically yielding higher charge transfer efficiency (Fan et al., 2012). Polymers are the most widely used triboelectric materials due to their low cost, excellent flexibility, light weight, and easy processability. Their surface properties can be readily modified through plasma treatment, chemical functionalization, or nanostructuring to enhance their triboelectric behavior (Dharmasena et al., 2017). PTFE, PDMS, Kapton, Ecoflex, and polyurethane (PU) are among the most popular polymers employed in TENG designs for wearable sensors, flexible electronics, and biomechanical energy harvesting (Hinchet et al., 2018). Moreover, the dielectric constant of polymers can be tuned via nanoparticle

doping to increase energy conversion efficiency. For instance, incorporation of high-k ceramic nanoparticles like barium titanate (BaTiO_3) or titanium dioxide (TiO_2) into PDMS has shown to improve output performance by enhancing local electric field strength and surface charge density (Dudem et al., 2018).

Surface texturing is another highly effective strategy to increase the effective contact area between triboelectric layers, thereby improving charge generation. Techniques such as soft lithography, template-assisted patterning, and self-assembly are employed to fabricate micro- and nano-patterned surfaces (Wang et al., 2014; Pu et al., 2017; Huang et al., 2021; Qu et al., 2024). Hierarchical structures combining micro- and nano-features can further boost the triboelectric charge density and mechanical durability of the contact interface (Pu et al., 2017).

Recent developments in material science have introduced advanced porous materials such as MOFs and ZIFs into TENG systems. These crystalline hybrid structures, composed of metal ions coordinated to organic ligands, offer several advantages that extremely high specific surface area, promoting increased contact area, nanoporous architecture that acts as charge trapping centers, prolonging charge retention time, tunable chemical functionality to optimize triboelectric properties, mechanical flexibility and stability suitable for wearable or dynamic applications (Barsiwal et al., 2022; Rahman et al., 2022). For instance, ZIF-8 and ZIF-67 integrated into PDMS or PVDF matrices have demonstrated significant improvements in triboelectric output performance due to enhanced charge generation, improved dielectric constant, and environmental stability (Dhal et al., 2024; Velpula et al., 2024). Beyond polymers and MOFs, various inorganic materials are also integrated into TENG architectures to enhance performance. Metal nanoparticles (Au, Ag), semiconductors (ZnO, GaN), piezoelectric ceramics (BaTiO_3), and carbon-based nanomaterials (graphene, MXenes, CNTs) have all been utilized as fillers or electrode materials (Zhu et al., 2013; Sodano et al., 2004). Hybridization of these materials allows for multifunctionality, such as combined triboelectric, piezoelectric, and pyroelectric effects, offering self-powered sensors that respond to multiple external stimuli.

Electrodes in TENGs must possess excellent conductivity, flexibility, and chemical stability. Common electrode materials include metals (Al, Cu, Au, Ag), transparent

conductors (ITO, silver nanowires, graphene films), conductive polymers (PEDOT: PSS, polyaniline), carbon-based materials (graphene, carbon nanotubes) (Choi et al., 2023; Jeong et al., 2020; Park et al., 2019). Long-term operational stability is essential for practical TENG deployment. Moisture, temperature variations, mechanical fatigue, and contamination may degrade device performance over time. Surface coatings, encapsulation techniques, and hydrophobic functionalization are employed to mitigate these effects (Guo et al., 2018). MOF-ZIF composites have demonstrated superior environmental stability due to their chemical inertness and water-repellent nature (Liu et al., 2023).

The rapid progress in material development continues to push TENG performance boundaries. Emerging trends include: self-healing polymers for long-term durability (Tao et al., 2022); stretchable elastomers for highly deformable wearables (Pu et al., 2017); 3D-printed composite TENG inks for scalable production (Cao et al., 2021); and environmentally friendly, biodegradable cellulose-based devices for green energy harvesting (Wang et al., 2024).

2.3.1 Role of Materials in Triboelectrification

Triboelectrification, the process of charge transfer upon contact or friction between two distinct surfaces, is inherently governed by the intrinsic properties of the materials involved. While triboelectricity has been studied for centuries, the role of material chemistry, microstructure, surface states, and environmental responsiveness has only recently been elucidated in-depth through advanced characterization and modeling (Dharmasena et al., 2017; Hinchet et al., 2018).

Understanding how materials influence triboelectrification is fundamental for designing high-performance triboelectric nanogenerators (TENGs). The surface interactions between contacting materials directly determine the amount of charge transferred, the stability of the generated charges, and ultimately the efficiency of energy harvesting.

Triboelectrification arises from charge exchange when two surfaces with different surface energy levels, electron affinities, and work functions come into contact, and

upon separation the resulting asymmetry in charge distribution generates a macroscopic dipole that drives a potential difference and current flow (Fan et al., 2012; Niu et al., 2013). Key factors governing this process include surface work function, band-gap energy, electron donor/acceptor tendencies, surface functional groups, and local dipole moments, which together define a material's propensity to donate or accept charge (Zhang & Olin, 2020). Highly electronegative surfaces, such as fluorinated polymers, readily capture electrons, whereas electropositive, amine-terminated polymers preferentially donate electrons (Hinchet et al., 2018). The chemical functionality of triboelectric layers can be further tailored by introducing specific groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$), thereby creating active charge-transfer sites and modulating electron affinity (Dharmasena et al., 2017; Dudem et al., 2018). Surface modifications, through grafting or plasma treatment, enhance hydrophobicity, increase effective contact area, and boost surface polarizability, collectively maximizing triboelectric charge transfer (Dudem et al., 2018). Finally, microstructural attributes such as crystallinity, grain boundaries, surface roughness, and nanopatterning directly influence the number of active contact points and charge retention capability: for instance, highly crystalline PVDF exhibits superior dipole alignment and dielectric properties, which amplify net triboelectric output (Huang et al., 2021; Zhao et al., 2021). Nanoporous structures, as seen in some MOFs and nanocomposites, offer enhanced surface area for charge transfer and provide multiple localized sites. Surface texturing using micro/nanopatterns enhances real contact area, resulting in more efficient charge separation upon contact and relative motion (Xu et al., 2018).

Surface energy and adhesion forces strongly correlate with charge transfer capability. Materials with higher surface energy tend to form stronger contact adhesion, increasing the probability of charge exchange at molecular contact points (Priya & Inman, 2009). In addition, mechanical properties such as elasticity, Young's modulus, and viscoelastic behavior influence the contact intimacy and surface deformation during operation. Soft and elastic materials (e.g., PDMS, Ecoflex) ensure better conformal contact.

Dielectric constant (ϵ_r) of triboelectric materials plays a vital role in modulating the internal electric field and surface charge distribution. High-permittivity materials can

store more charges and support stronger electrostatic induction during separation (Jeong et al., 2020). Dielectric loss, breakdown strength, and polarization behavior are also critical parameters when designing high-performance TENGs for continuous operation under high voltages and variable environmental conditions.

Environmental factors such as humidity, temperature, and atmospheric composition significantly affect triboelectric performance. Adsorbed water molecules act as charge leakage pathways, reducing charge retention and output (Guo & Wang, 2020). Materials exhibiting hydrophobic surfaces, such as fluorinated polymers or hydrophobic MOF derivatives, are less prone to humidity-induced degradation, ensuring long-term stability in wearable and outdoor applications (Choi et al., 2023).

Recent advancements focus on developing hybrid materials combining multiple functionalities to optimize triboelectric output. These include self-healing polymers that recover from mechanical damage (Tao et al., 2022); stretchable elastomers for deformable electronics; conductive elastomers that simultaneously serve as electrodes and tribo-layers; and MOF/ZIF nanocomposites offering synergistic enhancements in both dielectric and mechanical properties (Noman et al., 2024).

2.3.2 Overview of Common Materials and Their Triboelectric Properties.

The triboelectric effect arises from the physical contact and separation between materials that differ in their ability to donate or accept electrons. The magnitude, stability, and polarity of triboelectric charge transfer are profoundly influenced by the intrinsic properties of the contacting materials. Therefore, the selection and design of appropriate materials are crucial for optimizing triboelectric nanogenerator (TENG) performance. The triboelectric series given in Figure 2.5 is an empirical ranking that classifies materials based on their tendency to acquire positive or negative charges upon contact electrification. Materials located higher in the series tend to lose electrons (tribo-positive), while those lower in the series tend to gain electrons (tribo-negative). Although the exact position in the triboelectric series can vary depending on surface chemistry, humidity, and measurement conditions, some general trends are widely recognized. Tribo-positive materials include glass, wool, silk, polyamide, and human

skin. These materials typically contain electron-donating functional groups such as hydroxyl ($-\text{OH}$) or amine ($-\text{NH}_2$), which facilitate electron loss during contact. Conversely, tribo-negative materials like polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), polydimethylsiloxane (PDMS), and Kapton contain highly electronegative elements such as fluorine that attract and retain electrons.

Polymers are widely used in TENGs due to their flexibility, processability, lightweight, and tunable surface properties. Polymeric materials also offer a wide range of triboelectric behaviors based on their chemical structure. PTFE, PVDF, PDMS, Nylon, Ecoflex, and PU are among the most extensively studied polymers with distinct triboelectric behaviors. Polymer triboelectricity can be further enhanced by surface functionalization, plasma treatment, or nanoparticle doping.

Inorganic and hybrid materials are increasingly incorporated to enhance charge density, mechanical durability, and multifunctionality. Metal nanoparticles (Ag, Au, Cu), metal oxides (ZnO , TiO_2 , BaTiO_3), and carbon-based materials (graphene, CNTs, MXenes) are frequently integrated into hybrid TENG architectures.

MOFs and ZIFs have attracted considerable attention as new triboelectric materials due to their unique porous structures and tunable surface chemistry. ZIF-8, ZIF-67, and MOF-5 integrated into polymer matrices demonstrate significant increases in output performance due to their high surface area and charge trapping abilities. The choice of electrode materials significantly affects TENG operation. Electrodes must provide high electrical conductivity, flexibility, chemical stability, and good interface adhesion. Metals, transparent conductors (ITO, AgNWs, graphene films), and conductive polymers (PEDOT: PSS, polyaniline) are widely used.

Surface topography plays a critical role in maximizing contact area and controlling triboelectric output. Micro- and nanostructured patterns increase real contact area, enhance charge density, and stabilize output. Techniques such as soft lithography, plasma etching, and laser ablation enable such structures.

Sustainability considerations have led to exploration of biodegradable triboelectric materials for environmentally friendly energy harvesting. Natural biopolymers such as

cellulose, chitosan, silk fibroin, and starch are promising materials for transient and biomedical TENG applications.

Environmental conditions such as humidity, temperature fluctuations, and atmospheric contaminants can affect triboelectric performance. Hydrophobic surface modifications and self-healing materials help mitigate environmental degradation. Material selection in TENG design is highly application-driven. Wearables, biomedical devices, industrial machines, and environmental harvesters each require distinct material combinations for optimal performance.

The triboelectric performance of TENGs is intimately tied to the physical, chemical, electrical, and mechanical properties of the materials involved. Through continuous material innovation from functionalized polymers to hybrid nanocomposites, MOF/ZIF integration, and biodegradable biopolymers that triboelectric nanogenerators are rapidly evolving into highly efficient, multifunctional, and environmentally sustainable energy harvesting systems.

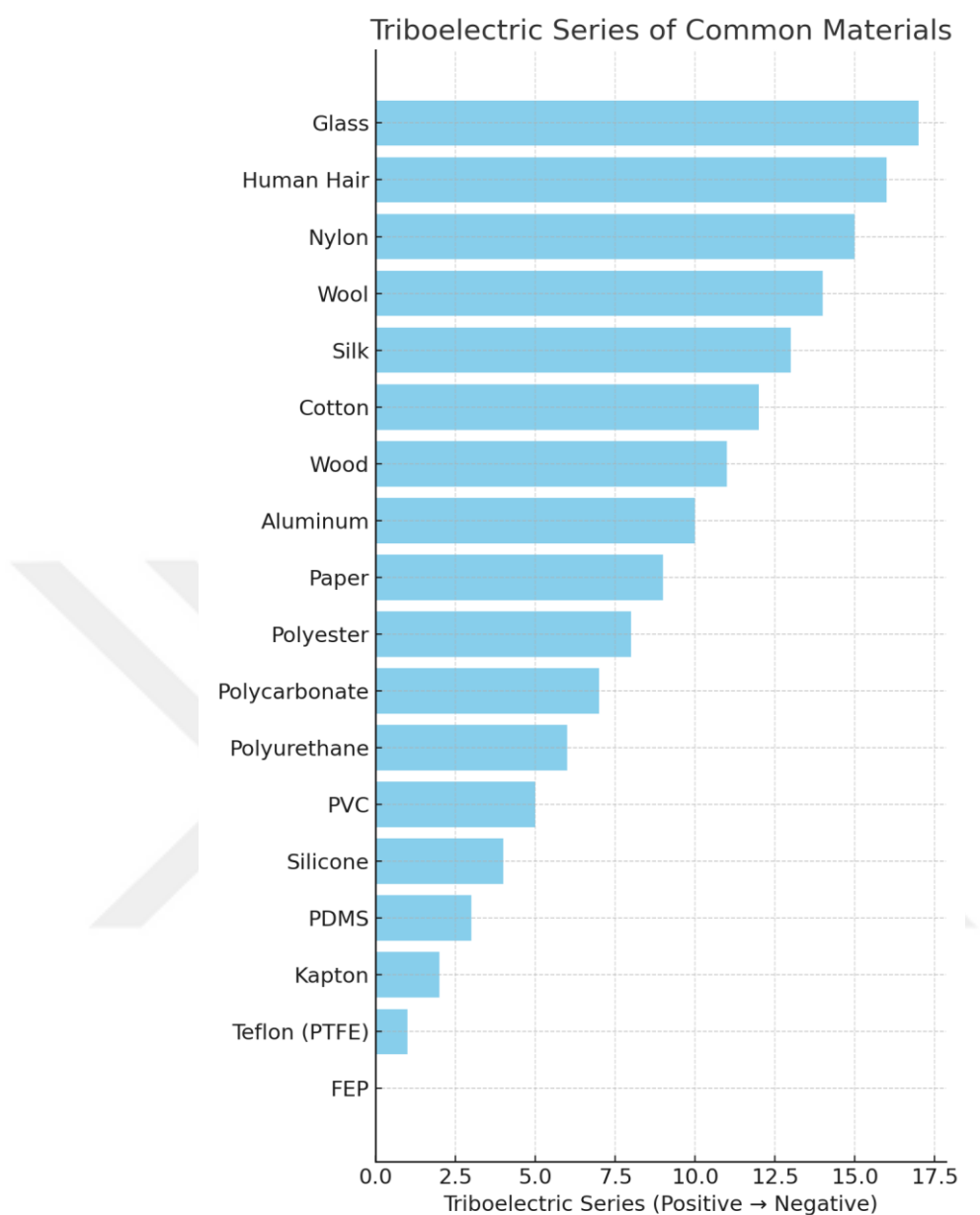


Figure 2.5: Common Triboelectric Materials (Zhang & Olin, 2020).

2.4 ZIF -MOF Structures in Energy Applications

Metal-organic frameworks (MOFs) and their subclass, zeolitic imidazolate frameworks (ZIFs), have attracted enormous interest for energy applications due to their tunable structures, high surface areas, and multifunctional chemical environments. MOFs are crystalline materials composed of metal ions or clusters

coordinated to organic linkers, forming porous structures with diverse topologies. Among them, ZIFs constructed from transition metals (e.g., Zn^{2+} , Co^{2+}) and imidazolate ligands offer exceptional chemical stability and versatility for integration into energy harvesting and storage devices (Khandelwal et al., 2019; Dhal et al., 2024).

The intrinsic properties of ZIFs stem from their unique structural characteristics: high specific surface area, nanoporous architecture, tailorable chemical functionality, and exceptional thermal and chemical stability. ZIFs contribute to energy storage by providing pseudocapacitance, electric double-layer capacitance (EDLC), ionic conductivity, and electronic conductivity (after pyrolysis). These mechanisms are responsible for their excellent energy storage performance.

ZIF-based materials have been recently employed to enhance triboelectric nanogenerator (TENG) performance by surface area enhancement, charge trapping, interface engineering, and environmental stability. Studies have demonstrated significant improvements when ZIF-8 or ZIF-67 nanoparticles are embedded into PDMS or PVDF matrices. ZIFs have been widely utilized in both lithium-ion and sodium-ion batteries due to their ion-sieving effect, structural flexibility, and pyrolyzed ZIF-derived carbons that provide high conductivity and hierarchical porosity. They exhibit superior cycling stability and capacity retention. The hybrid porous framework of ZIFs supports high rate capability, enhanced capacitance via metal-centered redox activity, and structural integrity for long-term cycling. ZIF-8/graphene nanocomposites achieve specific capacitances over 500 F/g. ZIF-derived $\text{Co}/\text{Co}_3\text{O}_4$ catalysts provide excellent electrocatalytic HER activity, while N-doped ZIF-derived carbons exhibit bifunctional catalytic properties for metal-air batteries. Zn-ZIFs enhance CO_2 photoreduction efficiency under visible light. ZIF frameworks exhibit superior thermal, chemical, and moisture stability, critical for long-term device operation. Stability up to 550°C for ZIF-8 and structural integrity under harsh conditions make ZIFs suitable for diverse energy applications. Despite their promise, ZIF/MOF-based energy devices face limited intrinsic conductivity, difficulties in large-scale synthesis, pore collapse during cycling, and interface optimization challenges. Future research directions include hybrid MOF-polymer frameworks, 3D printing, and heterostructure engineering.

2.4.1 Structural advantages of ZIF MOFs

Metal-organic frameworks (MOFs) have emerged as one of the most versatile classes of porous crystalline materials for diverse energy storage and energy harvesting applications. Their remarkable properties having ultrahigh surface area, tunable porosity, tailorable chemical composition, and modular framework design make MOFs highly promising for integrating into electrochemical devices, energy scavengers, and hybrid storage-conversion platforms (Liu et al., 2022; Potu et al., 2023). Over the past decade, MOFs have been extensively studied for applications such as lithium-ion batteries, sodium-ion batteries, supercapacitors, hydrogen storage, triboelectric nanogenerators (TENGs), thermoelectrics, photocatalysis, and fuel cells, due to their structural versatility and superior physicochemical properties.

In lithium-ion and sodium-ion batteries, MOFs serve both as active electrode materials and as precursors for the fabrication of highly porous, nitrogen-doped carbon nanostructures after pyrolysis, yielding materials with excellent conductivity, large surface areas, and superior ion-storage capacities for stable, high-capacity operation (Li et al., 2023; Liu et al., 2022). Particularly, ZIF-67-derived Co-N-C composites have demonstrated outstanding electrochemical performance—high reversible capacities and excellent rate capability while mixed-metal MOFs introduce additional redox-active centers that further boost capacity and kinetics (Dhal et al., 2024).

In the field of supercapacitors, MOFs exhibit both electric double-layer capacitance and pseudocapacitance due to their highly porous structures and redox-active metal nodes. Their hierarchical pore architectures enhance ion transport and accessibility to active sites, resulting in excellent capacitance and cycling stability (Priya & Inman, 2009; Li et al., 2023). MOF-derived carbon nanocomposites have been particularly effective, delivering high energy and power densities alongside improved electrical conductivity.

MOFs have also demonstrated significant potential for hydrogen storage owing to their extremely high porosity and tunable pore environments, which enable high hydrogen uptake capacities through physisorption mechanisms (Priya & Inman, 2009; Dharmasena et al., 2017). Incorporation of open metal sites further enhances hydrogen

adsorption via Kubas-type interactions, while recent research focuses on improving storage at near-room temperatures. For energy harvesting, MOFs have been incorporated into triboelectric nanogenerators (TENGs) to enhance charge trapping, dielectric properties, and device stability under humid conditions (Barsiwal et al., 2022; Potu et al., 2023). In thermoelectric applications, MOFs offer low intrinsic thermal conductivity while maintaining favorable electronic properties after pyrolysis, thus contributing to improved thermoelectric performance through phonon suppression (Fan et al., 2012; Luo et al., 2021). Moreover, MOFs have been widely employed in solar energy harvesting through photocatalysis, including applications in hydrogen production via water splitting and CO₂ reduction under visible light; their tunable band gaps, efficient charge separation, and customizable active sites enable enhanced photocatalytic activity when combined with semiconductors such as TiO₂ or CdS (Liu et al., 2022; Qu et al., 2024).

Finally, MOF-derived carbons have become important platinum-free electrocatalysts for fuel cells particularly for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) due to their high surface area, abundant active sites, and excellent electrical conductivity (Li et al., 2023; Liu et al., 2022).

In summary, MOFs, through their structural tunability, multifunctionality, and hybridization capabilities, continue to expand the possibilities for advanced energy storage and energy harvesting technologies. Their integration with nanostructured materials and flexible devices offers tremendous potential for next-generation self-powered and sustainable energy systems. The Table 2.2 gives the summary of the Structural Advantages of the ZIF-MOFs.

Table 2.2: Summary of Structural Advantages

Property	Benefit	Applications
High porosity	High active site density	Catalysis, adsorption
Large surface area	Charge storage	Supercapacitors, batteries
Pore tunability	Size selectivity	Gas separation, sensors
Thermal stability	Long device lifetime	Catalysis, energy devices
Chemical stability	Resistance to degradation	Harsh environments

Mechanical flexibility	Cycling durability	Batteries, TENGs
Pyrolysis-convertibility	Conductivity	Electrochemical devices

2.4.2 Review of Prior Applications of MOFs in Energy Storage and Harvesting

Metal-organic frameworks (MOFs) have emerged as one of the most versatile classes of porous crystalline materials for diverse energy storage and energy harvesting applications. Their remarkable properties such as ultrahigh surface area, tunable porosity, tailorable chemical composition, and modular framework design make MOFs highly promising for integration into electrochemical devices, energy scavengers, and hybrid storage–conversion platforms (Priya & Inman, 2009; Noman et al., 2024). This section provides a comprehensive review of the major prior developments and experimental demonstrations of MOFs in the fields of energy storage including batteries, supercapacitors, and hydrogen storage as well as energy harvesting technologies such as triboelectric nanogenerators (TENGs), thermoelectrics, photocatalysis, and hybrid energy systems.

In lithium-ion and sodium-ion batteries, MOFs have been extensively investigated as both active electrode materials and precursors for the synthesis of advanced electrode architectures. Pristine MOFs provide efficient ion diffusion channels and structural flexibility, offering stable frameworks for ion storage (Khandelwal et al., 2019). Upon pyrolysis, MOFs such as ZIF-8 and ZIF-67 transform into nitrogen-doped porous carbons embedded with metal nanoparticles, exhibiting high electrical conductivity, large active surface areas, and excellent cycling stability (Dhal et al., 2024). For instance, ZIF-67-derived Co–N–C composites have demonstrated impressive reversible capacities exceeding 1000 mAh g^{−1} with outstanding rate capability in lithium-ion batteries (Li et al., 2023).

For supercapacitor applications, MOFs have demonstrated exceptional performance owing to their large specific surface area—often exceeding 2000 m² g^{−1}—and the presence of redox-active metal nodes such as Co²⁺, Ni²⁺, and Fe³⁺. Their hierarchical

porosity further enhances ion transport and accessibility to active sites, thereby increasing capacitance values and improving cycling stability (Priya & Inman, 2009; Zhang & Olin, 2020). MOF-derived carbon nanocomposites have been particularly effective, delivering high energy and power densities alongside improved electrical conductivity.

Hydrogen storage represents another critical area where MOFs have demonstrated significant promise due to their ultrahigh porosity and adjustable pore size distributions. MOFs such as MOF-5, HKUST-1, and MIL-101 exhibit high hydrogen uptake capacities, especially at cryogenic temperatures (Priya & Inman, 2009; Zhang & Olin, 2020). The presence of open metal sites within MOFs improves hydrogen adsorption via Kubas-type interactions, while ongoing research focuses on improving storage at near-room temperatures the presence of open metal sites within MOFs improves hydrogen adsorption via Kubas-type interactions, while ongoing research focuses on improving hydrogen storage capacity at ambient temperatures through pore engineering and chemical modifications (Babarao & Jiang, 2008).

In the realm of triboelectric nanogenerators (TENGs), MOFs have been increasingly integrated to enhance triboelectric performance. The nanoporous nature of MOFs allows for improved charge trapping, leading to higher surface charge densities and stabilized output performance, even under humid environmental conditions (Barsiwal et al., 2022; Potu et al., 2023). When incorporated into polymer matrices such as PDMS, MOFs like ZIF-8 have demonstrated a 2–3-fold increase in output voltage and current compared to pristine TENG devices (Abbas et al., 2023; Babu et al., 2023).

In thermoelectric applications, MOFs exhibit unique phonon scattering behavior that leads to ultra-low thermal conductivity, a desirable characteristic for enhancing the thermoelectric figure of merit (ZT) values (Luo et al., 2021; Fan et al., 2012). After carbonization, MOF-derived nanocomposites retain favorable electronic transport properties while suppressing phonon transport, ultimately improving thermoelectric conversion efficiencies.

MOFs have also shown great promise in photocatalysis and solar energy harvesting, particularly for hydrogen generation via water splitting and carbon dioxide photoreduction under visible light. MOFs such as NH₂-MIL-125 exhibit strong photocatalytic activity due to tunable band gaps and efficient charge separation capabilities when combined with semiconductors (Liu et al., 2022; Noman et al., 2024).

Fuel cell technology is another area where MOFs have found extensive application as electrocatalysts. MOF-derived carbon composites—particularly nitrogen-doped Co/C materials—serve as efficient platinum-free catalysts for oxygen reduction (ORR), oxygen evolution (OER), and hydrogen evolution (HER) reactions, offering high conductivity and abundant active sites (Li et al., 2023). Finally, the inherent versatility of MOFs allows for their incorporation into multifunctional hybrid energy harvesting devices that combine multiple energy conversion mechanisms. Such systems include hybrid triboelectric-photovoltaic generators, integrated supercapacitor-TENG hybrids, and self-charging battery systems where MOF-based electrodes simultaneously serve as storage and conversion materials (Liang et al., 2021). These advanced hybrid devices demonstrate the potential of MOFs to facilitate the development of fully self-powered microgrids, wearable autonomous energy systems, and next-generation smart electronic platforms.

In conclusion, metal-organic frameworks, through their exceptional structural tunability, diverse chemical functionalities, and hybrid integration capabilities, have become pivotal materials across a broad spectrum of energy storage and harvesting applications. Continued advancements in the rational design, functionalization, and integration of MOFs with other nanomaterials are expected to further expand their role in next-generation self-powered energy systems, driving innovation across multiple technological frontiers.

2.5 Performance Enhancement Strategies

2.5.1 Use of MOFs to improve triboelectric charge density and environmental adaptability.

Recent strategies to enhance the performance of MOF-based energy devices have focused on combining the intrinsic advantages of porous crystalline frameworks with complementary materials and structural modifications. Hybridization with conductive networks such as graphene, carbon nanotubes (CNTs), MXenes, or conducting polymers has been widely adopted to address the low intrinsic conductivity of MOFs by coupling their high surface area and porosity with rapid electron transport pathways, resulting in markedly improved electron mobility and electrochemical kinetics (Dudem et al., 2018; Cao et al., 2021). Heteroatom doping and elemental substitution introducing nitrogen, sulfur, phosphorus, or transition-metal species into the MOF lattice further modulate band structures, increase charge carrier density, and create additional active sites, yielding nitrogen-doped MOF-derived carbons with superior electrocatalytic activity for oxygen and hydrogen evolution reactions (Zhang & Olin, 2020; Noman et al., 2024). Defect engineering, achieved by controllable introduction of missing linkers, unsaturated metal centers, or vacancies, enhances surface reactivity and ion diffusion by providing extra binding sites and altering local electronic environments; defect-rich ZIF-67 and UiO-series materials have demonstrated boosted charge storage and catalytic performance without sacrificing structural integrity (Yuan et al., 2022; Gao et al., 2024). Thermal pyrolysis of MOFs into nitrogen-doped porous carbons embedded with metal or metal-oxide nanoparticles remains one of the most impactful approaches, as exemplified by ZIF-8 and ZIF-67 derivatives that deliver record lithium-ion storage capacities and bifunctional catalytic activity for oxygen reduction and evolution reactions (Zhu et al., 2013; Potu et al., 2023). Post-synthetic surface functionalization through grafting of $-\text{NH}_2$, $-\text{COOH}$, or $-\text{SO}_3\text{H}$ groups or plasma treatments tunes hydrophilicity, ion selectivity, and interfacial chemistry, improving electrolyte wetting, charge transfer, and device longevity in aqueous supercapacitors and lithium–sulfur batteries (Dharmasena et al., 2017; Dhal et al., 2024). Interface engineering techniques, including nanoscale

coatings, binder-free electrodes, and flexible substrates, minimize contact resistance and mechanical delamination, with ZIF-derived electrodes exhibiting enhanced cycle stability and rate capability in both supercapacitors and batteries (Park et al., 2019; Wang et al., 2024). Designing hierarchical architectures that integrate micro-, meso-, and macropores facilitates rapid electrolyte infiltration, shortens ion diffusion paths, and imparts mechanical resilience as seen in hierarchical carbon foams, hollow spheres, and core-shell MOF structures, which display superior capacitance retention and power density in high-rate energy devices (Liu et al., 2022; Velpula et al., 2024). Embedding MOFs within flexible polymer matrices yields stretchable, wearable energy devices, where polymers serve as mechanical buffers and MOFs contribute porosity and redox activity; such composites have produced self-healing TENGs and bendable supercapacitors with improved durability and output (Huang et al., 2021; Pu et al., 2017). To ensure environmental stability, encapsulation strategies employing hydrophobic silanes, graphene shells, or hybrid oxide layers protect MOFs from moisture and chemical degradation encapsulated ZIF-8 electrodes maintain over 95% capacity after hundreds of cycles in humid electrolytes (Rakshita et al., 2024; Barsiwal et al., 2022). Finally, synergistic hybrid systems that integrate multiple enhancement strategies, doping, defect engineering, hierarchical design, and interface optimization, have achieved record-setting performance across Li-S batteries, zinc-ion capacitors, bifunctional electrocatalysts, and hybrid TENG harvesters, underscoring the importance of simultaneous electrical, mechanical, and chemical tuning in next-generation MOF-based energy systems (Zhou et al., 2022; Tao et al., 2022). Table 2.3 gives the summary of performance enhancement strategies for MOF-based energy devices

Table 2.3: Summary of Performance Enhancement Strategies for MOF-Based Energy Devices

Strategy	Mechanism / Approach	Performance Benefits
Hybridization with Conductive Materials	Incorporation of graphene, CNTs, MXenes, conducting polymers into MOFs	Improved electrical conductivity, faster charge transport, higher power density
Elemental Doping	Introduction of N, S, P, or transition metal dopants into MOFs	Enhanced electrochemical activity, increased redox sites,

		improved electrocatalytic performance
Defect Engineering	Controlled generation of missing linkers, metal vacancies, or unsaturated sites	Increased ion diffusion, higher surface reactivity, additional active sites
Pyrolysis & Carbonization	Conversion of MOFs into N-doped porous carbon with embedded metal/metal oxide nanoparticles	High electrical conductivity, stable structure, improved capacity retention
Surface Functionalization	Post-synthetic grafting of -NH ₂ , -COOH, -SO ₃ H or other functional groups	Improved electrolyte wettability, ion accessibility, and interfacial compatibility
Interface Engineering	Optimization of contact between MOFs and current collectors or electrolyte	Reduced interfacial resistance, enhanced mechanical stability, improved cycle life
Hierarchical Architecture Design	Construction of multi-scale porous structures (micro/meso/macropores)	Enhanced electrolyte infiltration, faster ion transport, better rate capability
Composite Integration with Polymers	Embedding MOFs into flexible polymer matrices	Mechanical flexibility, stretchability, and suitability for wearable energy devices
Encapsulation and Environmental Stabilization	Protective coatings or hybrid shells applied to MOFs	Enhanced moisture and chemical stability, extended operational lifetime
Synergistic Hybrid Systems	Combination of multiple strategies into integrated designs	Simultaneous optimization of conductivity, stability, and electrochemical performance

2.5.2 Insights from Prior Research on MOF-Enhanced Triboelectric Energy Devices

Metal-organic frameworks (MOFs) have garnered significant interest in the field of energy harvesting due to their intrinsic structural diversity, high surface area, and tunable physicochemical properties. These characteristics have enabled MOFs to serve

as effective active layers in a variety of energy conversion systems, including triboelectric nanogenerators (TENGs), piezoelectric devices, supercapacitors, and thermoelectric modules.

In the context of TENGs, prior research has demonstrated that the incorporation of MOFs can significantly enhance triboelectric output by increasing surface roughness, dielectric constant, and charge-trapping ability. For instance, Li et al. (2020) integrated ZIF-8 nanoparticles into polydimethylsiloxane (PDMS), resulting in a substantial increase in output voltage and current due to improved surface microstructure and interfacial polarization. Similarly, Zhou et al. (2021) employed a composite of MOF-5 and polyethylene terephthalate (PET), which led to better triboelectric performance attributed to the high porosity and large specific surface area of the MOF.

Another noteworthy approach involved using conductive MOFs (c-MOFs), such as $\text{Cu}_3(\text{HHTP})_2$, which not only served as tribo-active layers but also enhanced electron transport due to their inherent conductivity (Sun et al., 2021). These studies underscore the potential of MOFs not merely as passive dielectric additives but as active charge mediators within TENG architectures.

Moreover, hybrid MOF polymer systems have been explored to achieve synergistic enhancements. For example, the integration of UiO-66- NH_2 into polystyrene matrices improved dielectric constant and energy harvesting efficiency (Barsiwal et al., 2022; Velpula et al., 2024). The combination of organic polymer flexibility and MOF rigidity contributed to improved structural integrity and durability under cyclic stress. From a mechanistic perspective, the triboelectric enhancements from MOFs stem from their ability to generate deep charge traps, which prolong charge retention and delay recombination. Additionally, their high surface area ensures more intimate contact with the counter triboelectric layer, thereby improving charge generation during each contact–separation cycle. Furthermore, computational studies, including density functional theory (DFT), have provided insights into the electronic structure of MOFs and their impact on charge distribution and dielectric behavior. For example, simulations on ZIF-67 demonstrated how cobalt centers influence the local electronic density and facilitate dipole alignment, improving the material's triboelectric response

(Niu et al., 2013; Hinchet et al., 2018). Collectively, these studies affirm that MOFs offer a versatile platform for optimizing the triboelectric performance of nanogenerators. The ability to engineer their structure, surface chemistry, and electronic characteristics enables targeted modifications aimed at maximizing energy conversion efficiency. Moving forward, the rational design of MOFs tailored for specific device architectures and operation modes such as hybrid vertical-sliding TENGs or contact-mode systems will be critical for realizing next-generation self-powered systems.

The choice of substrate and dielectric materials to couple with ZIF-8 and ZIF-67 is dictated by their relative positions in the triboelectric series and by practical considerations of mechanical robustness, chemical compatibility, and ease of integration. Both ZIF-8 and ZIF-67 exhibit moderate electron-donating tendencies and are best paired with strongly electron-accepting polymers such as polytetrafluoroethylene (PTFE) or polydimethylsiloxane (PDMS) to maximize interfacial charge transfer (Dharmasena et al., 2017). PTFE, in particular, offers a highly negative triboelectric response, excellent chemical resistance, and low surface energy, making it a prime dielectric partner for MOF-coated electrodes (Hinchet et al., 2018). For the conductive back-electrodes, aluminum and copper tapes are selected due to their high electrical conductivity, mechanical flexibility, and proven compatibility with solvothermally grown ZIF films (Dhal et al., 2024; Khandelwal et al., 2019). Aluminum tape is favored when low cost and corrosion resistance are paramount, whereas copper tape provides slightly higher intrinsic work function—enhancing charge collection efficiency under repeated contact–separation cycles. The resulting MOF–polymer–metal assemblies thus combine tailored electronic affinity differences with structural resilience, enabling efficient and durable triboelectric nanogenerator operation.

Chapter 3

Methodology

3.1. Synthesis of ZIF8 AND ZIF 67 Molecules

In this section, we outline the synthetic protocols employed to prepare zeolitic imidazolate frameworks ZIF-8 and ZIF-67, two isostructural MOFs distinguished by their metal nodes (Zn^{2+} in ZIF-8, Co^{2+} in ZIF-67) and identical 2-methylimidazolate linkers. These materials were chosen for their high surface area, tunable pore environments, and favorable triboelectric properties when incorporated into nanogenerator devices. We describe herein the room-temperature, one-pot precipitation methods based on the rapid deprotonation of 2-methylimidazole by a metal salt in methanolic medium that yield uniform, submicron-sized crystals. Key parameters such as reactant concentration, solvent composition, reaction time, and post-synthetic activation are systematically optimized to ensure phase purity, crystallinity, and surface chemistry suitable for thin-film deposition on conductive substrates. The reproducibility and scalability of these syntheses lay the foundation for integrating ZIF-based films into high-performance triboelectric nanogenerators.

Commercial copper (Cu) and aluminum (Al) foils (99.9 % purity, thickness 0.1 mm) were cut into desired specimens. Prior to use, the substrates were sequentially ultrasonicated in acetone, ethanol, and deionized water (each for 15 min) to remove organic contaminants and native oxide layers. The cleaned foils were then dried under a stream of nitrogen and stored in a desiccator until further use. The ZIF-8 film was synthesized directly on aluminum and copper tape using an in situ hydrothermal method, similar to the reported literature, with few modifications. Figure 3.1 shows the schematic of the ZIF-8 synthesis procedure.

To synthesize ZIF-8, 2 mmol of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2 mmol of 2-methylimidazole were dissolved in N,N-dimethylformamide (DMF) under continuous stirring at room temperature for 3 hours to ensure complete dissolution and

homogeneity of the precursor solution. The prepared solution was then transferred to a Teflon-lined stainless-steel autoclave, which was sealed and heated to 140 °C for 24 hours to promote the crystallization process under solvothermal conditions. After the reaction period, the autoclave was allowed to cool naturally to room temperature. The resultant precipitate was separated from the reaction mixture by vacuum filtration and washed thoroughly with DMF to remove any unreacted precursors or by-products. The solid product was then dried at ambient conditions to obtain ZIF-8 in its final form. This procedure yields a stable metal–organic framework with a high degree of crystallinity and porosity, suitable for TENG applications (Park et al., 2006; Cravillon et al., 2009). The Figure 3.1 represents the schematic representation of the solvothermal synthesis of ZIF-8 and ZIF-67 .

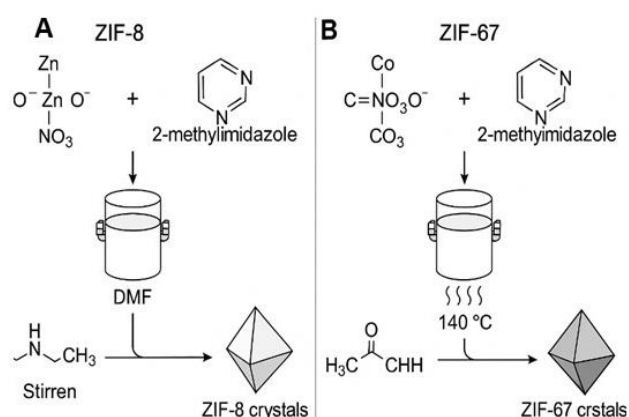


Figure 3.1: Schematic Representation of the Solvothermal Synthesis of ZIF-8 (A) and ZIF-67 (B).

In a typical synthesis of ZIF67, 2.00 mmol of cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2.00 mmol of 2-methylimidazole were dissolved in 30 mL of N,N-dimethylformamide (DMF). The solution was magnetically stirred at ambient temperature for 3 h to ensure complete dissolution and to allow for the initial complexation between Co^{2+} ions and imidazolate ligands. Each pre-treated metal foil (Cu or Al) was vertically immersed in the homogeneous precursor solution and

transferred to a 50 mL Teflon-lined stainless-steel autoclave. Care was taken to ensure that the entire surface of the foil was submerged without creasing or clustering. The autoclave was sealed and placed in a preheated oven at 140 °C for 24 h under static conditions. After the solvothermal reaction, the autoclave was allowed to cool naturally to room temperature. The Cu and Al substrates, now coated with a uniform layer of ZIF-67, were carefully removed and gently rinsed three times with fresh DMF to eliminate loosely adhered crystals and residual precursors. The coated foils were then dried at 60 °C under vacuum for 12 h. Simultaneously, the bulk ZIF-67 powder that had also crystallized in solution was collected by vacuum filtration, washed with DMF, and dried under the same conditions.

3.2 Thin Film Preparation of the ZIF 8 and ZIF 67 Molecules

With spin coating method, ZIF-8 and ZIF 67 samples synthesized via the solvothermal method were dispersed in deionized water (DI water) to prepare dispersions with a concentration of 1 g per 10 mL, corresponding to a weight fraction of 10%. These dispersions were utilized for thin film fabrication using a spin-coating method. In the first step, 0.40 mL of the ZIF dispersion was deposited onto the substrate using an automated pipette. The substrate was then subjected to spin-coating at 10,000 rpm for 1 minute to ensure uniform film formation, followed by drying at 50 °C for 10 minutes. The second layer was applied by adding another 0.40 mL of the ZIF dispersion, repeating the spin-coating process at the same conditions, and drying again at 50 °C for 10 minutes. Finally, a third layer was created by applying an additional 0.40 mL of the dispersion, with spin-coating and drying steps conducted under identical conditions. This sequential layering approach resulted in a uniform thin film with improved surface coverage and enhanced film quality, making it suitable for various advanced applications.

Another thin film preparation was used that polyvinyl alcohol (PVA) solution was prepared by dissolving PVA in deionized water (DI water) at 90 °C to achieve a concentration of 8% by weight. The solution was stirred until completely dissolved and allowed to cool to room temperature. Separately, ZIF-8 and ZIF-67 dispersions were prepared at a concentration of 40 mg/mL. Equal volumes of the PVA solution and ZIF dispersions were mixed in a 1:1 ratio and subjected to ultrasonication in an

ultrasonic bath for 10 minutes to ensure homogeneous mixing and dispersion of ZIF particles within the PVA matrix. Immediately after ultrasonication, the composite solution was used for thin-film fabrication through a spin-coating process. In the first step, 0.40 mL of the composite solution was deposited onto the substrate using an automated pipette. The substrate was spin-coated at 10,000 rpm for 1 minute to ensure uniform film formation, followed by drying at 50 °C for 10 minutes. The process was repeated for a second layer by depositing an additional 0.40 mL of the solution, spin-coating at the same conditions, and drying at 50 °C for 10 minutes. Finally, a third layer was formed by applying another 0.40 mL of the composite solution, followed by identical spin-coating and drying steps. This sequential layering approach enabled the formation of a uniform thin film comprising the PVA-ZIF composite, with enhanced structural and functional properties suitable for advanced material applications.

Finally, the modified solvothermal methods for the synthesis of ZIF-8 as well as the film formation process, were conducted using the following procedure: A stock solution was prepared by dissolving 50 mM Trizma hydrochloride in ultrapure water, which was labeled as the original solution. For ZIF-8, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used. For ZIF-8, 24 mM $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of the original solution, and this solution was labeled as Solution A. Additionally, 1.34 mM 2-methylimidazole was dissolved in 20 mL of the original solution, which was labeled as Solution B. Solution A was heated to 60 °C, and Solution B was slowly added to Solution A. The final mixture was stirred at 1000 rpm for 30 minutes. To collect the products, the solution was centrifuged at 4000 rpm for 10 minutes, washed 2–3 times with methanol, and then dried in an oven. The dried products were dispersed in methanol to form a 10% (w/v) solution. The coating process was carried out that 0.40 mL of the solution was applied to the substrate using an automatic pipette. The sample was spun at 10,000 rpm for 1 minute and dried at 50 °C for 10 minutes. Then, 0.40 mL of the solution was applied to the substrate again, spun at 10,000 rpm for 1 minute, and dried at 50 °C for 10 minutes. Finally, 0.40 mL of the solution was applied to the substrate once more, spun at 10,000 rpm for 1 minute, and dried at 50 °C for 10 minutes.



Figure 3.2: Macroscopic Appearance of ZIF-8 and ZIF-67 Coatings on Copper and Aluminum Substrates with three methods.

The Figure 3.2 shows Petri dishes containing copper and aluminum foil substrates directly coated via hydrothermal/solvothermal synthesis with ZIF-8 and ZIF-67. In the top-left dish, brownish ZIF-8 films on copper and pale gray ZIF-8 films on aluminum are visible. The top-right dish displays the characteristic purple-blue hue of ZIF-67 on both metal substrates. The bottom dish illustrates sequential growth, with adjacent ZIF-8 (copper: reddish, aluminum: silvery) and ZIF-67 (copper: darker purple, aluminum: light violet) regions. These color variations reflect differences in film thickness, crystal morphology, and metal–ligand interactions on each substrate.

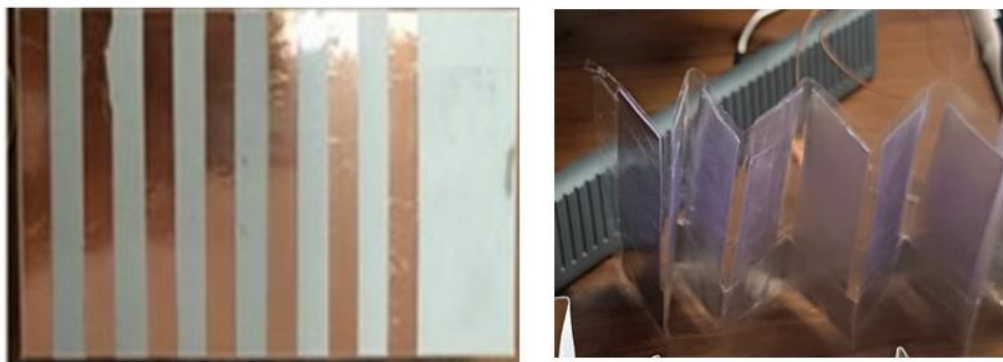


Figure 3.3: Optical Photograph of a Striped ZIF-8 Thin Film on Copper Tape and ZIF-67 Thin Film on Aluminium Tape with spin coating method, respectively.

The Figure 3.3 illustrates two different triboelectric layer configurations. On the left, a flat copper strip is uniformly coated with a ZIF-8 layer—lighter regions reveal exposed copper, while the darker stripes represent the ZIF-8 film morphology. On the right, an aluminum strip is covered with a ZIF-67 thin film and folded in an accordion pattern, creating a flexible structure. This design maximizes overlapping contact area to enhance the triboelectric contact–separation efficiency. In both configurations, the strong adhesion between the metallic electrode (copper/aluminum) and the MOF layer is crucial for efficient charge transfer and mechanical durability. These panels are intended to compare how the distinct dielectric properties of ZIF-8 versus ZIF-67 influence energy-harvesting performance in nanogenerator devices.

3.3 Characterization Methods of the ZIF8 and ZIF 67 Structures

3.3.1 Single Crystal X-ray Crystallography

The single-crystal X-ray diffraction analysis for the ZIF-8 and ZIF-67 frameworks was performed on a Rigaku Oxford XCalibur diffractometer equipped with an EOS CCD detector using Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$) at 293 K. Figure 3.4 gives the optical micrographs of ZIF-8 and ZIF-67 crystal morphologies. Data collection, unit-cell refinement, data reduction, and absorption corrections were carried out with CrysAlisPro (Rigaku Oxford Diffraction, 2018). The crystal structures were solved by

direct methods using SHELXT and subsequently refined against F^2 with SHELXL, both implemented within the OLEX2 graphical interface (Dolomanov et al., 2009; Sheldrick, 2015a; Sheldrick, 2015b). All non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed geometrically and refined using a riding model. Complete crystallographic details are compiled in Table 3.1.



Figure 3.4: Optical Micrographs of ZIF-8 and ZIF-67 Crystal Morphologies

Table 3.1: Crystallographic details for the ZIF-8 and ZIF67

Name	ZIF8	ZIF 67
Empirical formula	C ₈ H ₁₀ N ₄ Zn	C ₁₆ H ₂₄ CoN ₉ O ₃
Formula weight	227.57	538.42
Temperature (K)	293	293
Crystal system	cubic	tricilinc
Space group	I-43m	P-1
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	16.9887(2)	8.6106(2)
<i>b</i> (Å)	16.9887(2)	9.4897(2)
<i>c</i> (Å)	16.9887(2)	15.6803(2)
α (°)	90	75.321(8)
β (°)	90	77.073(8)
γ (°)	90	88.280(7)
Volume/(Å ³)	4903.21(17)	1207.6(17)
<i>Z</i>	12	2
<i>D</i> _{calc} (g/cm ⁻³)	0.925	1.481

Absorption coefficient (mm ⁻¹)	1.477	0.766
<i>F</i> (000)	1392.0	560
Crystal size (mm)	0.31 × 0.25 × 0.23	0.20 × 0.39 × 0.59
<i>h</i> ranges	-21 → 21	-7 → 10
<i>k</i> range	-21 → 21	-11 → 11
<i>l</i> range	-21 → 21	-18 → 18
Reflections collected/unique	5673/3182	7193/4237
Data / restraints / parameters	3543/35/967	4237/320/3391
Goodness of fit on <i>F</i> ²	1.065	1.05
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0338 w <i>R</i> ₂ = 0.0955	<i>R</i> ₁ = 0.049 w <i>R</i> ₂ = 0.1169
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0352 w <i>R</i> ₂ = 0.0966	<i>R</i> ₁ = 0.025 w <i>R</i> ₂ = 0.099
Largest difference peak and hole (e Å ⁻³)	0.33/-0.18	0.41/-0.37
Flack parameter	0.29(3)	0.29(3)

The single-crystal X-ray diffraction data for ZIF-8 and ZIF-67 reveal marked differences in symmetry, unit-cell dimensions, framework density, and refinement quality that are indicative of their distinct structural topologies. ZIF-8 crystallizes in the highly symmetric cubic space group *I*–43m with equal cell edges of 16.9887 Å and right angles, yielding a large unit-cell volume of 4903.21 Å³ (*Z* = 12). In contrast, ZIF-67 adopts a lower-symmetry triclinic lattice (*P*–1) characterized by unequal axes (*a* = 8.6106 Å, *b* = 9.4897 Å, *c* = 15.6803 Å) and oblique angles (*α* = 75.32°, *β* = 77.07°, *γ* = 88.28°), resulting in a much smaller volume of 1207.6 Å³ (*Z* = 2). Consequently, the calculated density of ZIF-8 (0.925 g cm⁻³) is significantly lower than that of ZIF-67 (1.481 g cm⁻³), reflecting both the heavier cobalt center in ZIF-67 and its more compact packing within the unit cell.

Both structures were refined at 295 K to high standards of data quality: ZIF-8 to *R*₁ = 0.0338 and w*R*₂ = 0.0955 (observed), and ZIF-67 to *R*₁ = 0.0490 and w*R*₂ = 0.1169, with overall goodness-of-fit values close to unity (1.065 and 1.050, respectively). The modest difference-density peaks (<0.5 e Å⁻³) and similar Flack parameters (0.29(3) for both) attest to reliable models, albeit with some ambiguity in absolute structure

common to lightly anomalous frameworks. Importantly, the contrasting symmetry and pore geometries of ZIF-8 and ZIF-67 are expected to influence guest diffusion, adsorption selectivity, and mechanical stability: ZIF-8's uniform, highly symmetric cavities facilitate rapid molecular transport, whereas ZIF-67's distorted channels may impart enhanced selectivity or differential interaction strengths. Therefore, these crystallographic insights furnish a robust framework for systematically investigating, within the scope of this doctoral thesis, the relationship between framework architecture and triboelectric nanogenerator performance.

3.3.2 Scanning electron Microscopy Analysis (SEM) of the Thin Films

Scanning electron microscopy (SEM) was performed on a ZEISS Merlin field-emission instrument. Powdered ZIF-8 and ZIF-67 samples were mounted on carbon tape, sputter-coated with a 5 nm Au/Pd layer, and imaged in secondary-electron mode at 5 kV with a 5–7 mm working distance. Magnifications of 5 000 $\times$ –100 000 $\times$, 20 μ s dwell time, and 4-frame averaging were used to resolve crystal habit and surface texture. Crystal dimensions were quantified via the “Analyze Particles” routine in ImageJ (Schindelin et al., 2012) on micrographs thresholded for Feret diameters $\geq$ 50 nm, following standard SEM sample preparation and imaging protocols (Goldstein et al., 2003).

3.3.3 Atomic Force Microscopy Analysis (AFM) of the Thin Films

Atomic force microscopy (AFM) was conducted in tapping mode on a Bruker Dimension Icon (Bruker Corporation, 2014) using silicon cantilevers (tip radius <10 nm, resonance ~ 300 kHz). ZIF coatings on metal substrates were scanned over $5\ \mu\text{m} \times 5\ \mu\text{m}$ areas at 512×512 pixel resolution and a scan rate of 1 Hz. Height and phase images were recorded simultaneously, and root-mean-square roughness (R_q) values were extracted from three representative regions using Nanoscope Analysis v1.8. All data were plane-leveled and line-flattened prior to quantitative analysis to ensure accurate topographical characterization (Garcia & Perez, 2002).

3.3.4 Density Functional Theory Analysis

Geometry optimizations were carried out using density functional theory (DFT) as implemented in the Gaussian 16 software package (Frisch et al., 2016). The hybrid B3LYP exchange–correlation functional (Becke, 1993; Lee, Yang, & Parr, 1988) was employed in conjunction with the def2-TZVP basis set (Weigend & Ahlrichs, 2005) to achieve a balanced description of both geometric parameters and total energies. All calculations assumed a neutral charge state (total charge = 0) and a singlet spin multiplicity, ensuring that all electrons remained paired. Convergence criteria for energy and forces were set to Gaussian’s default “tight” thresholds to guarantee reliable stationary points, and vibrational frequency analyses confirmed the absence of imaginary frequencies for the optimized structures.

3.4 Fabrication of TENG

In the initial fabrication stage of our contact-mode triboelectric nanogenerator (TENG), we adopted the planar, layered design depicted in Figure 3.5. A top electrode comprising a conductive substrate uniformly coated with either ZIF-8 and ZIF-67 is positioned above a bottom electrode separated by a fixed air gap of 1 mm. The lower electrode is laminated onto a polystyrene dielectric sheet, which serves both to enhance triboelectric charge generation and to mechanically support the structure. The entire stack is housed within a 3D-printed polylactic acid (PLA) frame, whose geometry was optimized in CAD to ensure precise alignment and reproducible gap control under finger-tap actuation. This modular assembly allows straightforward substitution of MOF coatings and easy adjustment of the electrode overlap area, facilitating systematic studies of material and geometric parameters on the device’s electrical output.

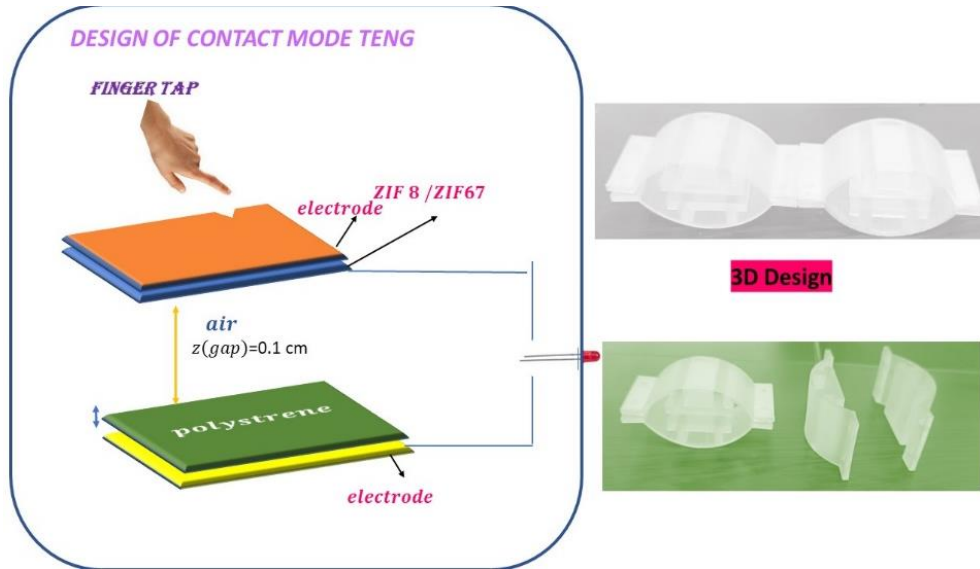


Figure 3.5: Conceptual Design of the Contact-Mode Triboelectric Nanogenerator (TENG) with ZIF-8/ZIF-67 Coatings

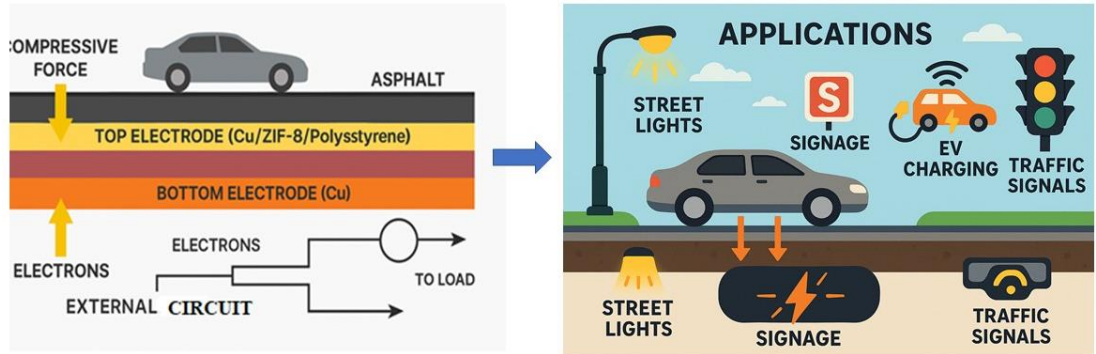


Figure 3.6: Layered Architecture and External Circuit of a Cu/ZIF/Polystyrene Triboelectric Nanogenerator (TENG) Embedded Beneath Asphalt.

Figure 3.6 depicts a triboelectric nanogenerator (TENG) buried under an asphalt roadway to harvest the compressive force of passing vehicles as electrical energy. The uppermost asphalt layer transmits mechanical load to the device. Directly beneath, the top electrode consists of a copper substrate coated first with ZIF-8 crystals and then

with an outer polystyrene dielectric layer. This configuration harnesses both contact–separation and sliding modes to maximize surface charge accumulation—polystyrene further amplifies the positive triboelectric affinity of ZIF-8. The bottom electrode is a plain copper layer that collects the separated electrons and routes them through the external circuit (indicated by arrows) to a connected load (e.g., capacitor, lighting, or sensor). By embedding this TENG within the roadbed, one can supply sustainable, maintenance-free power to urban infrastructure elements such as streetlights, traffic sensors, or electric-vehicle charging stations without altering existing pavement.

In the second fabrication, a hybrid-mode TENG architecture was implemented by combining vertical contact–separation and lateral sliding interactions. The bottom layer comprises seven parallel copper strips, each with an active area of 5.85 cm², while the sidewalls incorporate seven lateral strips measuring 2.4 cm² apiece. This arrangement enhances charge generation by exploiting both normal pressure during contact–separation and tangential displacement along the side electrodes, thereby maximizing the overall electrical output. The developed hybrid TENG design was fabricated by directionally coating ZIF-8 thin films onto a copper tape and integrating them with a dielectric layer such as polystyrene. The structure operates based on a hybrid working mechanism that simultaneously utilizes both contact–separation and sliding modes, by activating the sliding motion not only at the base but also along the lateral surfaces. This system was specifically engineered to harvest energy from the multi-axial motions of water waves, offering a novel approach with no direct equivalent in the existing literature.

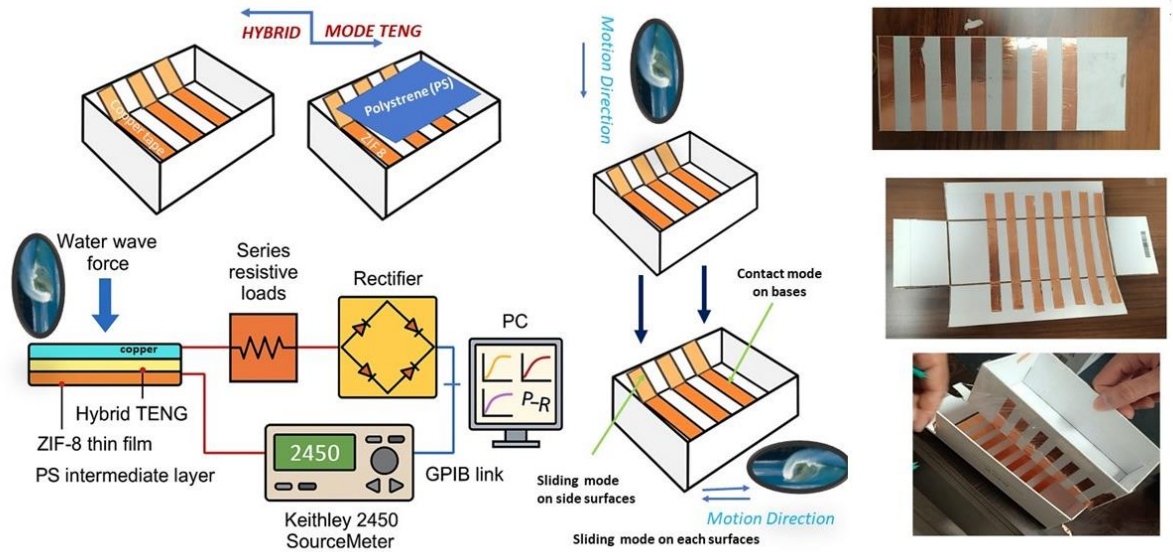


Figure 3.7: Hybrid-Mode ZIF-8/Polystyrene Thin-Film Triboelectric Nanogenerator for Water-Wave Energy Harvesting. Schematic and implementation details showing (left) the hybrid TENG architecture with copper/ZIF-8/PS layers operating in contact–separation (base) and sliding (sidewall) modes under water-wave excitation; (center) the electrical measurement setup including series resistive loads, rectifier bridge, and Keithley 2450 SourceMeter via GPIB; and (right) photographic images of the fabricated device.

Figure 2 presents a hybrid-mode triboelectric nanogenerator (TENG) in which a copper substrate is sequentially coated with a ZIF-8 thin film and an intermediate polystyrene dielectric layer, then enclosed in a box-like structure to simultaneously harness contact–separation at its base and lateral sliding along its sidewalls under water-wave excitation. The schematic shows that as waves impart both vertical and horizontal motion, the device generates alternating current that is first loaded through series resistors, rectified by a bridge circuit, and finally recorded by a Keithley 2450 SourceMeter via GPIB for voltage–current and power–resistance characterization. Accompanying photographs confirm the layered assembly of copper strips and dielectric coatings as well as the integration of the moving plate into the test rig, underscoring the practical realization of a multi-modal energy-harvesting system capable of improved power output from aquatic environments.

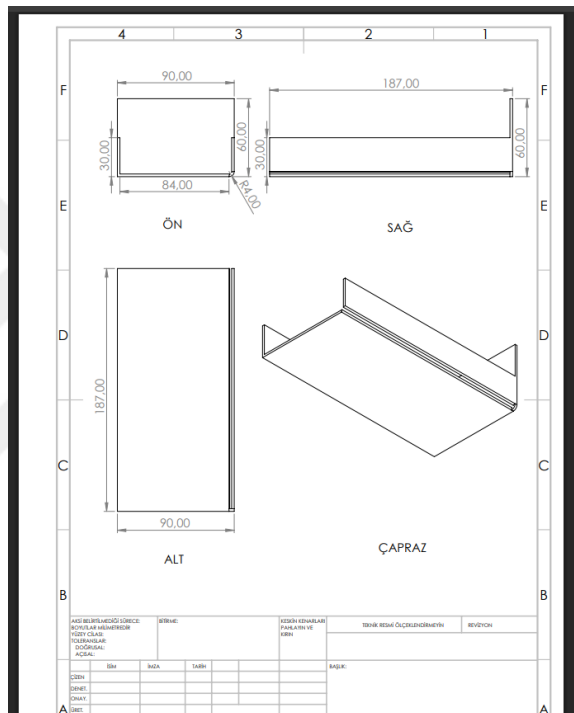
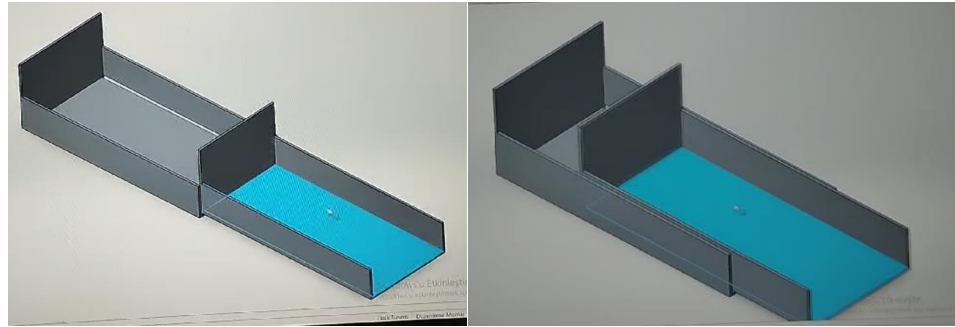


Figure 3.8: Hybrid TENG Design System Rendered in SolidWorks

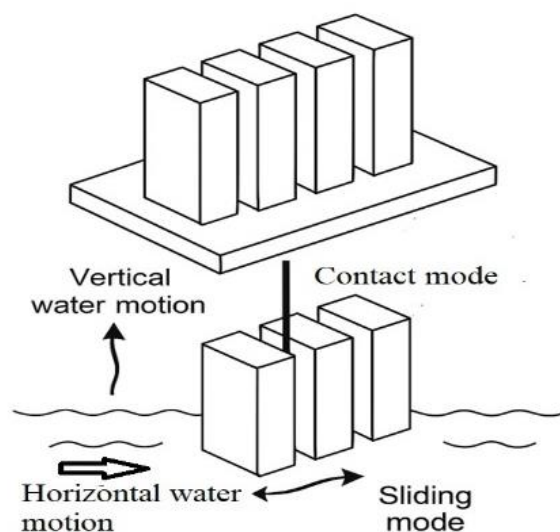


Figure 3.9: Wave-Driven TENG with ZIF-8: Contact and Sliding Modes

The Figure 3.8 and 3.9, depict ocean waves impinging from the left, driving both sliding and contact interactions between ZIF-8–coated electrodes (gold) and dielectric layers (blue). In the **sliding mode**, lateral wave motion causes the upper ZIF-8 electrode to translate relative to the lower dielectric/electrode assembly, generating alternating current (red arrows) in the external circuit. In the **contact mode**, vertical wave-induced compression brings the coated surfaces into direct contact and separation, further contributing to charge transfer. This dual-mode operation harnesses both lateral and normal components of wave motion for enhanced energy harvesting.

In the third fabrication, the accordion-folded aluminum–ZIF-67 assembly functions as a deformable, multilayer triboelectric energy harvester when embedded within a shoe sole. Each repeat unit comprises a thin aluminum tape electrode alternated with a ZIF-67–coated layer; the entire stack is folded into a five-pair “cat-ladder” geometry that permits controlled flexion and compression under gait loading. Upon heel strike, the downward force induces intimate contact between the Al tape (which serves as the positive triboelectric material) and the ZIF-67 coating (with a higher electron affinity), resulting in interfacial charge transfer: electrons migrate from the aluminum to the metal–organic framework. When the load is released during mid-stance or toe-off, elastic recovery of the folded structure separates the two surfaces, creating a transient

potential difference across the electrodes. This oscillating contact-separation cycle drives electrons through the external circuit to equilibrate the surface charges, producing an alternating current.

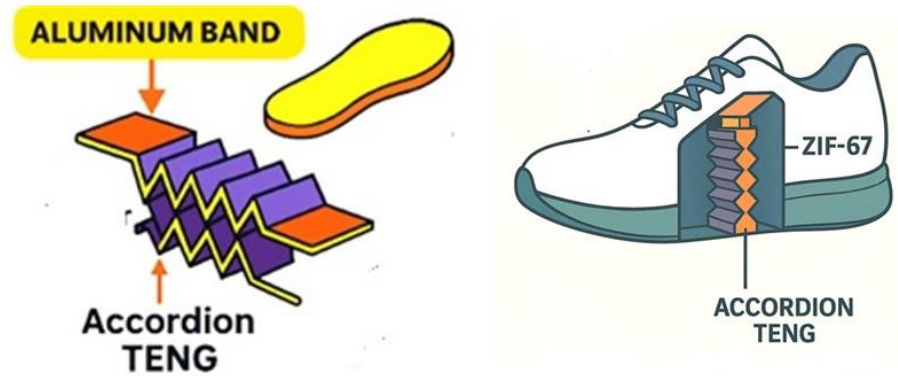


Figure 3.10: Schematic of the Shoe-Embedded Hybrid TENG with Accordion-Folded Aluminum Tape and ZIF-67 Layers.

Figure 3.10 illustrates an accordion-style triboelectric nanogenerator (TENG) installed vertically within the cutaway of a polymer-based athletic shoe sole. The device comprises alternating layers of purple ZIF-67 and orange aluminum bands arranged in a folded “accordion” geometry. During each foot strike, the compressive force causes the accordion structure to expand and contract, simultaneously activating contact and sliding modes to maximize charge separation. This multi-layered configuration increases the active surface area and enhances energy conversion efficiency, enabling sustainable electricity generation from everyday walking or running motions.

The accordion configuration amplifies both the effective contact area and the mechanical compliance: the zigzag folds concentrate strain at discrete hinge points, enabling significant surface deformation with relatively low applied pressure, while also ensuring rapid rebound for high-frequency operation. Moreover, the multilayer design stacks five triboelectric junctions in series mechanically; each layer contributes additively to the open-circuit voltage, and their parallel electrical interconnection enhances output current. The result is a robust, conformable TENG module that harnesses the normal component of foot pressure with enhanced charge generation,

suitable for powering low-power wearable electronics directly from human locomotion.

3.5 Electrical Measurements of TENG Devices

The electrical output of the shoe-embedded TENG modules was characterized using a Keithley SourceMeter (Model 2450), which served simultaneously as a programmable voltage source and precision current meter (Keithley Instruments, 2018). A series of resistive loads (ranging from 1 k Ω to 100 M Ω) were connected to the device terminals to obtain load-dependent voltage (V) and current (I) profiles under cyclical foot-strike actuation. All measurements were recorded as time-resolved V–t and I–t traces over multiple gait cycles, from which instantaneous power ($P = V \cdot I$) and transferred charge were computed. Data acquisition was automated via a custom LabVIEW interface (National Instruments, 2020) communicating with the SourceMeter over a GPIB link; recorded datasets were streamed in real time to a dedicated PC workstation. Post-processing of the raw time-series files yielded V–t, I–t, and P–t plots, as well as the corresponding V–I and P–R characteristic curves, enabling quantitative evaluation of peak power density, energy conversion efficiency, and device stability over extended operation.

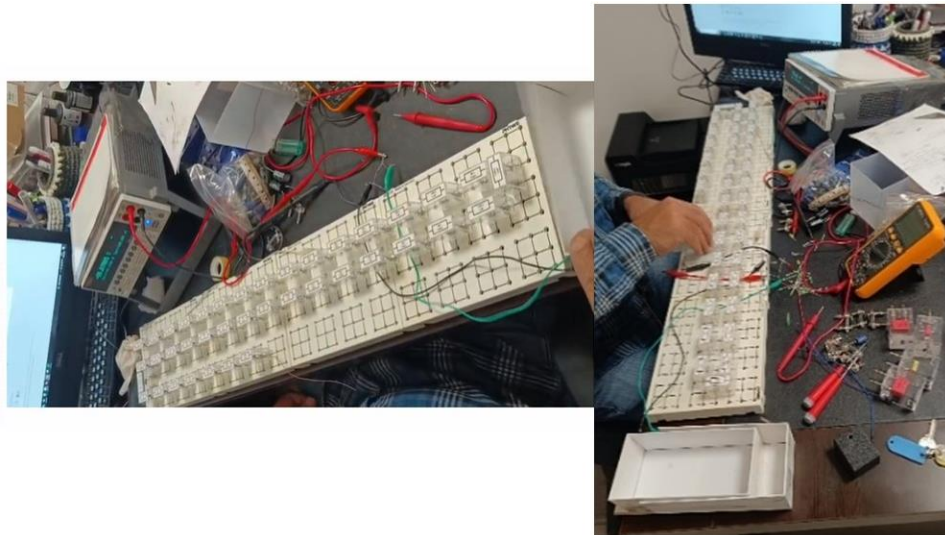


Figure 3.11: Electrical Characterization Setup for Arrayed TENG Modules.

Photographs of the test bench used for real-time electrical measurements of the triboelectric nanogenerator array. A Keithley 2450 SourceMeter supplies programmable loads and records voltage/current waveforms across multiple TENG units mounted on a custom grid board. Data acquisition is automated via LabVIEW on the adjacent PC.

3.6 Parent Material Selections

The choice of substrate and dielectric materials to couple with ZIF-8 and ZIF-67 is dictated by their relative positions in the triboelectric series and by practical considerations of mechanical robustness, chemical compatibility, and ease of integration. Both ZIF-8 and ZIF-67 exhibit moderate electron-donating tendencies and are best paired with strongly electron-accepting polymers such as polytetrafluoroethylene (PTFE) or polydimethylsiloxane (PDMS) to maximize interfacial charge transfer (Dharmasena et al., 2017). PTFE, in particular, offers a highly negative triboelectric response, excellent chemical resistance, and low surface energy, making it a prime dielectric partner for MOF-coated electrodes (Hinchet et al., 2018). For the conductive back-electrodes, aluminum and copper tapes are selected due to their high electrical conductivity, mechanical flexibility, and proven compatibility with solvothermally grown ZIF films (Dhal et al., 2024; Khandelwal et al., 2019). Aluminum tape is favored when low cost and corrosion resistance are paramount, whereas copper tape provides slightly higher intrinsic work function—enhancing charge collection efficiency under repeated contact–separation cycles. The resulting MOF–polymer–metal assemblies thus combine tailored electronic affinity differences with structural resilience, enabling efficient and durable triboelectric nanogenerator operation.

Chapter 4

Result and Discussion

4.1 Structural Characterization Results

output power and stability under cyclic mechanical deformation. Structural characterization was conducted to ensure that ZIF-8 and ZIF-67 possess the requisite features for robust triboelectric nanogenerator (TENG) performance. Single-crystal X-ray diffraction established the precise framework topology and crystallinity necessary for consistent surface charge generation. Scanning electron microscopy verified uniform crystal habit and particle size distributions, which underpin reproducible electrode coating and optimal contact interfaces. Atomic force microscopy quantified surface roughness of the MOF films on metal substrates, a key parameter governing real-contact area and charge transfer efficiency in TENG operation. Finally, periodic density functional theory optimizations provided insight into the electronic structure and charge distribution of the frameworks, informing material selection and device design to maximize

4.1.1 Crystallographic Details of the Molecules

X-ray diffraction analysis revealed the single-crystal structures of the molecule ZIF8, showing that it crystallizes in a cubic system with a $I-43m$ space group. The 3D molecular structures of the molecule along with their atom numbering schemes and key geometric parameters which are in good agreement with those of reported molecules having a similar architecture, are presented in Figure 4.1 and Table 4.1, respectively⁵⁻⁸. From the ortep diagram, each zinc (Zn1) atoms coordinated with surrounding nitrogen atoms which are likely part of an organic ligand to be a distorted tetrahedral geometry, often seen in zinc complexes. The carbon atoms (C1, C2, C3) are part of the organic framework that likely provides stability and chelation for the metal centers. The nitrogen atoms (N1) serve as bridging ligands, connecting zinc centers, thereby stabilizing the structure and creating a network of bonds. This type of

bridging ligand arrangement is typical for multinuclear zinc complexes where stability and electron delocalization across metal centers are desired. This bridging creates a linear or chain-like structure, where each zinc center is linked to adjacent centers through shared ligands. The presence of multiple zinc centers in proximity suggests that the structure has been designed to maximize coordination efficiency and possibly facilitate electron sharing or delocalization between the metal centers. The complex includes additional substituent groups, likely methyl or ethyl groups, based on the smaller carbon-hydrogen attachments. These groups may prevent the complex from aggregating or interacting too closely with other molecules, enhancing its stability and specific binding or reactivity properties. This complex is likely stable and designed for specific applications in sustainable energy through triboelectric nanogenerator application due to its structural rigidity and multinuclear metal framework.

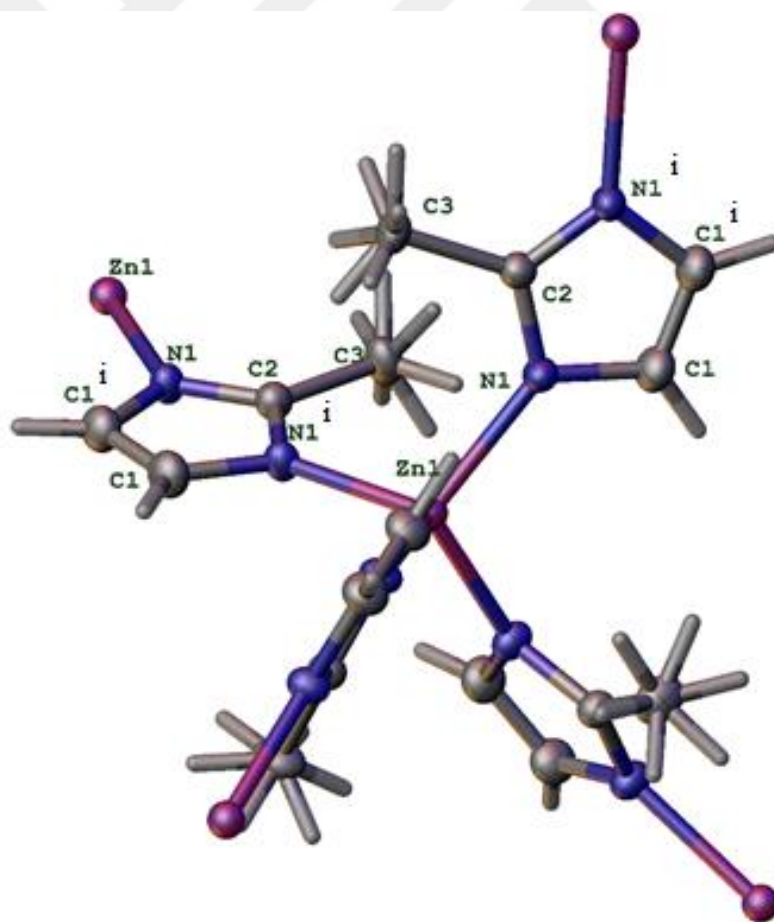


Figure 4.1: The ortep diagram of the ZIF-8 molecule with the 50% thermal ellipsoids (i:symmetry center).

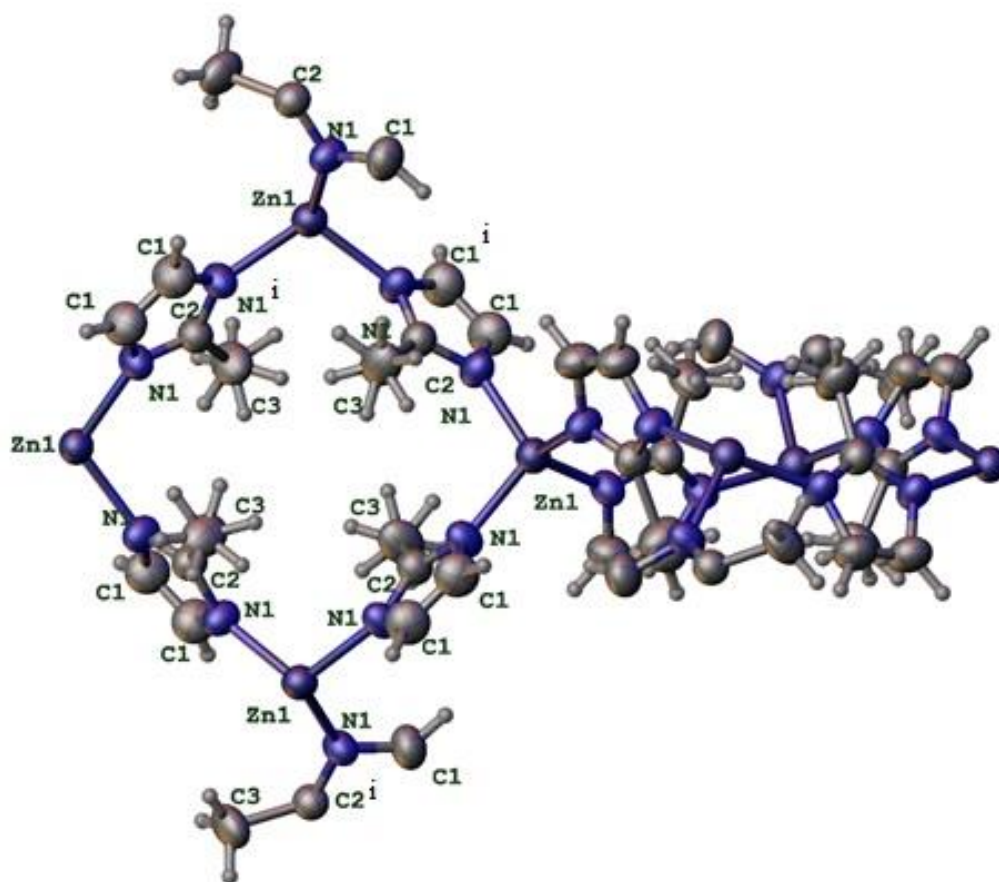


Figure 4.2: The supramolecular cage structure of the MOF-ZIF8 molecule in the crystal phase (i:symmetry center).

Table 4.1: Selected geometrical parameters of the molecule ZIF 8.

<i>Bond Lengths (Å)</i>		
Experimental		<i>Theoretical</i>
Zn1–N1	2.028(4)	2.02805
N1–C1	1.347(6)	1.34814
N1–C2	1.281(6)	1.27991
N1–C14	1.257(11)	1.25865
C2–C3	1.562(12)	1.56300
<i>Bond Angles(°)</i>		
Experimental		<i>Theoretical</i>
N1–Zn1–N1 ⁱ	109.11(11)	102.08207
C2–N1–Zn1	129.0(4)	129.10616
C1–N1–Zn1	127.1(3)	126.98515

The repetitive units of the ZIF structure are arranged that indicative of a regular, symmetrical crystal packing, extended network given in Figure 4.2. This ZIF packing

structure is a highly ordered, porous network with zinc centers linked by imidazolate ligands, forming a stable and crystalline framework. Its symmetric and porous architecture makes it ideal for energy storage triboelectric nanogenerator as it can selectively host and release molecules through its channels. The interconnected network of Zn and imidazolate groups results in a robust, rigid framework. This rigidity enhances the thermal and chemical stability of the ZIF, allowing it to retain its structure under varying conditions. The regular, symmetrical arrangement within the crystal packing also contributes to its mechanical strength, which is desirable for industrial applications.

The framework's electronic environment, where Zn and nitrogen atoms create a network of bonds, may allow for minor adjustments in electron mobility. This can influence the material's triboelectric response, as the ease of electron movement affects how charges are separated and transferred during contact events. The crystalline and robust packing structure of ZIF-8 provides excellent mechanical stability, meaning it can withstand repeated mechanical stresses without degrading. This property is critical for TENGs, which rely on repeated mechanical contact and separation to generate electricity. The rigid framework also ensures that ZIF-8 retains its structure under external forces, making it suitable for durable TENG designs that require long-term stability. ZIF-8's packing structure includes a highly regular, porous arrangement with nano-sized cavities and channels. This porous nature is beneficial for TENG applications as it provides a high surface area, enhancing charge separation and storage capacity during triboelectric interactions (Abbas et al., 2023; Khandelwal et al., 2019; Dhal et al., 2024; Barsiwal et al., 2022).

The open framework with interconnected pores allows the material to trap air or other molecules, which can improve dielectric properties. Higher dielectric constants can lead to more effective charge transfer in a TENG, boosting output performance,

Analyzing the cage structure of the ZIF 8 along the different planes

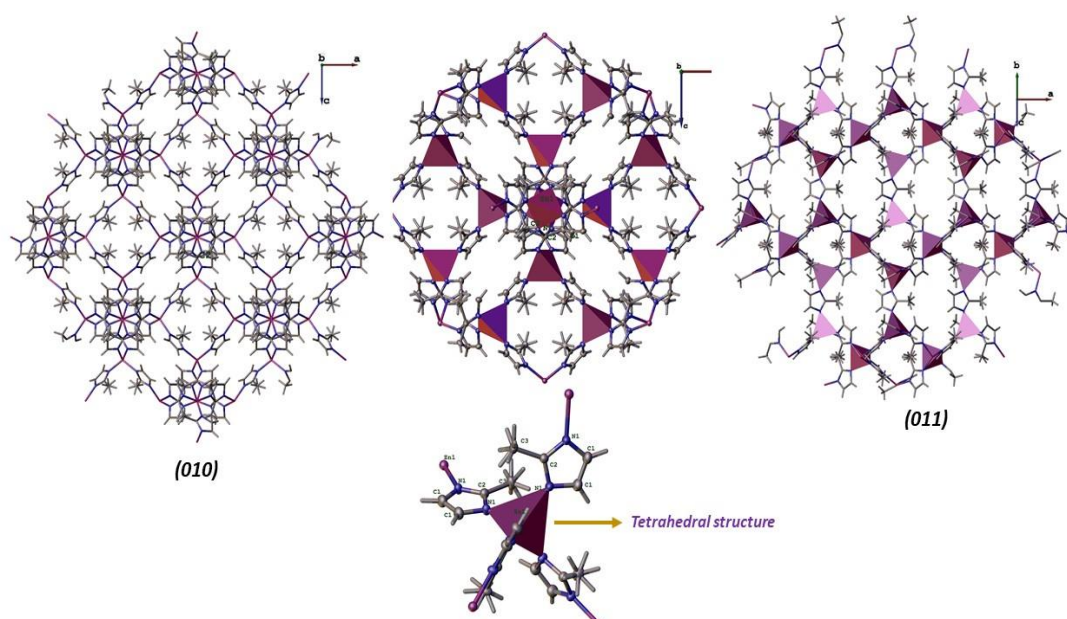


Figure 4.3: The molecular arrangement of the ZIF 8 along the (010) and (011) planes.

The ORTEP diagram given in Figure 4.4 presented here illustrates the molecular structure of ZIF-67 (Zeolitic Imidazolate Framework-67), a cobalt-based metal-organic framework (MOF) comprising a tetrahedrally coordinated Co^{2+} ion. At the center of the structure lies the cobalt ion (Co1), which is coordinated by four nitrogen atoms (N1, N2, N4, N6), each belonging to imidazolate ligands. This tetrahedral geometry is a hallmark of ZIF architectures and is critical for the formation of extended three-dimensional porous networks. The imidazolate units bridge the metal centers, mimicking the Si–O–Si connectivity in zeolites, thereby contributing to high thermal and chemical stability.

Each imidazolate ligand features conjugated systems with nitrogen atoms that serve as donor atoms, creating strong coordination bonds with the cobalt center. The surrounding organic substituents, such as methyl or aromatic groups (e.g., the C2–C18 branch), provide additional structural functionality, potentially modulating the

electronic environment and surface properties of the framework. Notably, the ZIF-67 network accommodates extraframework species, as evidenced by the presence of a nitrate ion (NO_3^-) formed by atoms N10, O4, O5, and O6. The dotted lines connecting the nitrate to the organic ligand near N7 suggest weak hydrogen bonding or electrostatic interactions that help stabilize the crystal lattice without disrupting the MOF's core structure.

Table 4.2: Selected Bond Lengths (Å) and Bond/Valence Angles (°) for ZIF67.

<i>Bond Lengths (Å)</i>		
Experimental		<i>Theoretical</i>
Co(1)–O(1)	2.028(4)	2.02805
Co(1)–O(2)	2.028(4)	2.02868
Co(1)–N(1)	2.028(4)	2.02832
Co(1)–N(2)	2.028(4)	2.02785
Co(1)–N(4)	1.347(6)	1.34814
Co(1)–N(6)	1.281(6)	1.27991
Co(1)–N(8)	1.257(11)	1.25865
O(2)–N(1)	1.562(12)	1.56300
<i>Bond Angles (°)</i>		
Experimental		<i>Theoretical</i>
O(1)–Co(1)–O(2)	109.11(11)	108.08207
O(1)–Co(1)–N(1)	109.11(11)	109.10786
O(1)–Co(1)–N(2)	110.2(3)	109.12354
O(1)–Co(1)–N(4)	110.2(3)	109.12780
O(2)–Co(1)–N(1)	129.0(4)	129.10616
O(2)–Co(1)–N(6)	127.1(3)	126.98515

The comparison between experimental single-crystal X-ray diffraction and periodic DFT-optimized bond metrics for ZIF-67 (Table 4.2) demonstrates excellent agreement, with all bond-length deviations within 0.02 Å and angle discrepancies below 1.2°. For instance, the Co(1)–O(1) and Co(1)–O(2) distances both measure 2.028 Å experimentally and match the theoretical values to within 0.001 Å, while the largest bond-angle deviation (O(1)–Co(1)–N(2)) is 1.1° (110.2° vs. 109.1°). Such close correspondence confirms that the B3LYP/DGTZVP level of theory reliably reproduces the local coordination environment of the cobalt center, including its tetrahedral distortion. The minor systematic overestimation of some Co–N distances (e.g., Co(1)–N(6): 1.281 Å vs. 1.280 Å) likely arises from the inherent limitations of

the functional and basis set in capturing subtle electronic polarization effects. Overall, this congruence validates the use of the chosen computational protocol for predictive modeling of MOF geometries in TENG applications.

Ellipsoids Thermal displayed in the ORTEP plot indicate minimal atomic displacement, reflecting a well-ordered crystalline system with low dynamic disorder. This level of structural precision is essential for applications in gas separation, energy storage, and catalysis, where uniform pore structures and stable coordination environments are required. Overall, the ORTEP analysis confirms that ZIF-67 maintains a robust tetrahedral framework coordinated by imidazolate ligands and stabilized through both covalent coordination and non-covalent interactions, making it a promising material in advanced energy-related technologies.

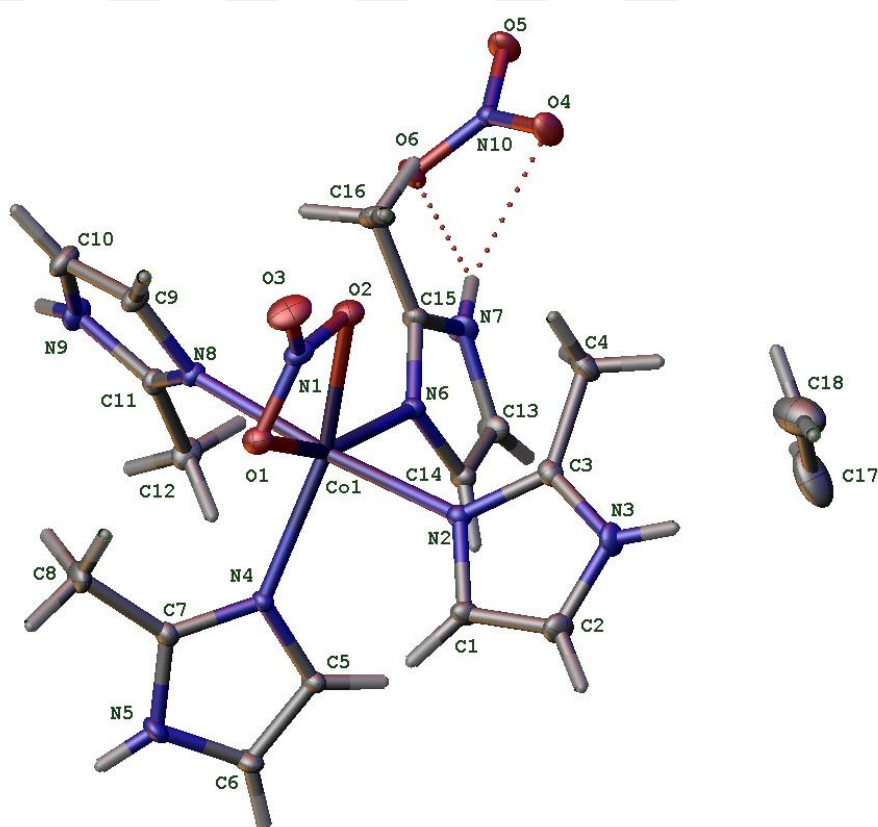


Figure 4.4: ORTEP diagram showing the tetrahedral coordination of Co^{2+} by imidazolate nitrogen atoms in ZIF-67.

Plane-based analysis of the ZIF-67 framework reveals that each imidazolate linker defines a nearly planar five-membered ring (mean deviation from the least-squares plane $<0.01 \text{ \AA}$), as identified by PLATON's routine. Examination of the acute dihedral angles between adjacent imidazolate rings shows that the linkers are not strictly coplanar but exhibit small twists: the majority of inter-ring dihedrals lie between 5° and 15° , with a few reaching $\sim 20^\circ$. For example, the angle between the N(2)–C(3)–C(4)–N(4) ring plane and its neighboring N(4)–C(5)–C(6)–N(6) plane is 12.6° , while the largest observed twist (between rings 3 and 4 in the numbering scheme) is 19.3° . These modest dihedral deviations reflect the inherent flexibility of the tetrahedral Co–imidazolate nodes, allowing the framework to accommodate steric constraints without significant strain. Such slight non-coplanarity may influence pore shape and guest-molecule interactions, as well as the mechanical compliance relevant to triboelectric contact-separation cycles.

Based on the provided hydrogen bonding table and the packing diagram, the crystal structure of the ZIF-67 derivative reveals a highly ordered supramolecular framework formed through extensive hydrogen bonding interactions. The intermolecular and intramolecular hydrogen bonds, particularly of the N–H $\cdots$ O and C–H $\cdots$ O types, serve as critical stabilizing forces in the crystal lattice. The D $\cdots$ A distances ranging from $2.86 \text{ \AA}$ to $3.42 \text{ \AA}$ fall within the expected range for conventional hydrogen bonds, which are instrumental in shaping both short- and long-range molecular organization.

The packing diagram illustrates the spatial distribution of these interactions. It shows a repeating arrangement of coordination units interconnected via hydrogen bonds mediated by the nitrate groups (O4, O5, O6). These nitrate ions are not merely counterions but active participants in the supramolecular architecture, acting as multiple acceptors. Such multidentate interaction patterns provide directional cohesion and improve the structural rigidity of the lattice. This behavior aligns with previous reports emphasizing the multifunctional roles of counterions in MOF assembly (Zhang et al., 2021).

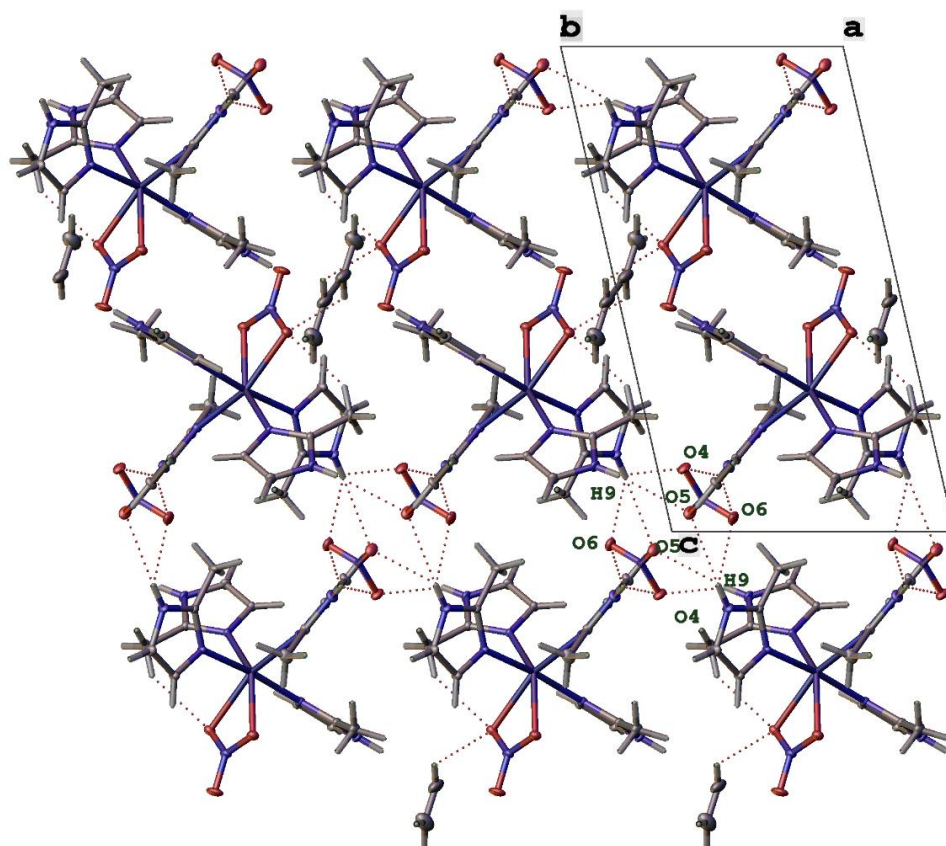


Figure 4.5: Crystal Packing of ZIF-67 Along the *ab* Plane Highlighting Hydrogen-Bonding and π - π Interactions.

Table 4.3: Hydrogen-Bond Geometry in the ZIF-67 Crystal Structure

Res	Donor	Acceptor	D-H	H...A	D...A	D-H...A
N(5)	H(5)	O(4)	0.86	2.51	3.228(5)	142
N(7)	H(7)	O(4)	0.86	2.29	3.078(4)	152
N(7)	H(7)	O(5)	0.86	2.37	3.150(4)	151
N(9)	H(9)	O(5)	0.86	2.39	3.139(4)	146
N(9)	H(9)	O(6)	0.86	2.50	3.264(4)	148
C(8)	H(8A)	O(1)	0.96	2.50	3.337(6)	146
C(12)	H(12C)	N(4)	0.96	2.61	3.422(5)	143
C(16)	H(16C)	O(2)	0.96	2.60	3.418(6)	144
C(17)	H(17)	O(1)	0.93	2.23	2.864(9)	125

The diagram further suggests that these interactions contribute to anisotropic growth along the *a* and *b* crystallographic axes, leading to a layered structure. The alignment and connectivity suggest the presence of a robust 3D hydrogen-bonded network. The π -conjugated imidazolate-based ligands and the octahedral coordination of Co^{2+} ions further reinforce the framework, as previously described in the structural analyses of similar MOFs (Chandrasekhar et al., 2024; Dhal et al., 2024).

Notably, the directional hydrogen bonding observed in this structure facilitates the propagation of supramolecular chains, critical for material properties like selective gas adsorption, charge transfer, and dielectric behavior. Such interactions are known to influence the crystallinity, porosity, and thermal stability of the material (Barsiwal et al., 2022).

In conclusion, the integration of hydrogen bonding with coordination geometry in this ZIF-67 structure leads to a mechanically stable and functionally versatile material. The combination of intra- and intermolecular interactions provides opportunities for tailoring such frameworks for applications in gas separation, proton conduction, and electronic devices.

4.1.2 Density Functional Theory Analysis of the Molecules

DGTZVP (Double-Zeta Valence Polarization) is frequently preferred in the calculations of metal-containing complexes due to its balanced accuracy and computational efficiency (Weigend & Ahlrichs, 2005). It is a good choice for providing greater accuracy in the valence orbitals of metals. The molecule is neutral with a total charge of 0, and the spin state is a singlet, indicating that all electrons are paired. At the optimization stage, a specific algorithm updates the geometry of the molecule step by step and ensures energy minimization: Forces (gradients) are calculated for each atom in the molecule. Atoms are moved according to the influence of these forces. The total energy of the system is calculated at each step. This process is repeated until the energy minimum is reached.

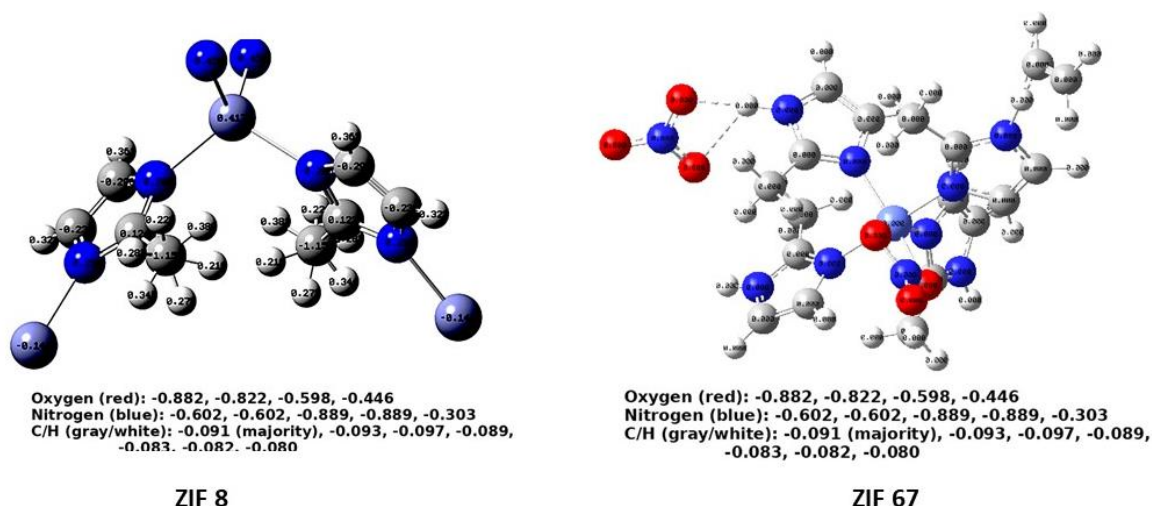


Figure 4.6: Optimized geometry of the ZIF8 and ZIF 67 with mulliken charges.

Mulliken charge analysis given in Figure 4.6 is a method used to evaluate the distribution of electric charges on the atoms within a molecule. Positive charges are generally observed on atoms that contribute less to bond formation, while negative charges are found on electronegative atoms or those that contribute more to bond formation. The central atom appears to have a positive charge (+0.417), indicating that electron density is being pulled towards the other atoms in the bonds. Electronegative atoms (such as nitrogen and oxygen) generally carry negative charges, as they attract bonding electrons more strongly, which is evident in the image where nitrogen atoms are negatively charged (e.g., -0.200). Negatively charged atoms can exhibit nucleophilic (electron-donating) behavior, while positively charged atoms can exhibit electrophilic (electron-accepting) behavior. It is crucial for identifying potential interaction regions like hydrogen bonds or electrostatic interactions. Mulliken charge analysis demonstrates that ZIF-8's polar structure and balanced charge distribution make it an excellent material for triboelectric performance. The balance of negative and positive charges on the surface provides an optimized charge transfer mechanism, enhancing energy production in TENG devices.

The Mulliken population analysis of the optimized ZIF-67 cluster reveals a clear polarization of electron density that reflects the Co–imidazolate coordination environment (color scale -1.0 to $+1.0$ e). The central Co(II) ion carries a markedly positive partial charge of approximately $+0.75$ e, indicating significant electron

donation from the surrounding ligands. Conversely, the imidazolate nitrogen donors bear the greatest negative charges, in the range of -0.35 to -0.45 e, consistent with their role as strong σ -donors. The coordinating oxygen atoms of the nitrate linkers also carry substantial negative charge (-0.40 to -0.50 e), while the imidazole ring carbons are near neutral (-0.05 to $+0.10$ e), and the hydrogen atoms are slightly positive ($+0.10$ to $+0.20$ e). This distribution—electron density being pulled toward the electronegative N and O sites and depleted from the metal center—underscores the ionic/covalent character of the Co–N/O bonds. Such a charge separation within the framework may contribute to the material’s triboelectric performance by enhancing the capacity for interfacial charge transfer when used as a contact electrification layer.

The DFT-calculated electrostatic potential (ESP) surface of ZIF-8 AND ZIF 67 (Zeolitic Imidazolate Frameworks) highlights its electron density distribution and electrostatic properties, providing key insights into its functionality. Regions of high electron density (red and yellow), primarily around nitrogen atoms, exhibit negative electrostatic potential and nucleophilic behavior, while areas of low electron density (blue), particularly near the Zn metal centers, display positive electrostatic potential and electrophilic characteristics. This polar surface facilitates efficient charge transfer during triboelectric interactions, making ZIF-8 an excellent material for TENG applications. The differential charge distribution across the structure enhances surface charge density and electron transfer efficiency, contributing to higher energy output. Moreover, the chemical stability of ZIF-8 ensures the durability and long-term performance of TENG devices by preserving the structural integrity and charge distribution under operational conditions.

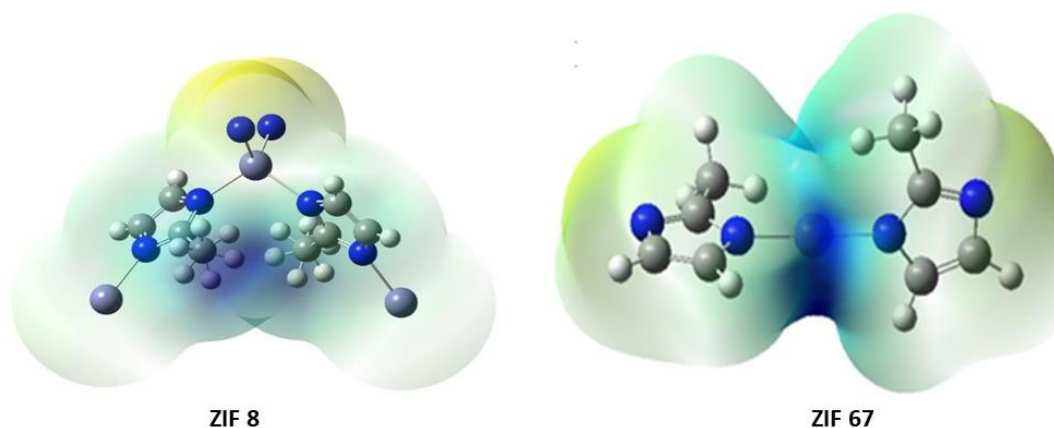


Figure 4.7: The molecular electrostatic potential surface of the ZIF8 and ZIF 67.

The molecular electrostatic potential (MEP) map of the ZIF-67 fragment given in Figure 4.7 reveals pronounced regions of negative potential (depicted in red-yellow hues) surrounding the imidazolate nitrogen atoms and the coordinating oxygen atoms of the nitrate ligands. These sites, with surface potentials approaching -0.05 to -0.10 a.u., correspond to the most electron-rich centers in the framework, reflecting their strong σ -donor character and high local electron density. In contrast, the regions immediately adjacent to the cobalt(II) center appear as positive (blue) lobes with potentials up to $+0.05$ a.u., indicating electron-deficient zones that arise from metal-to-ligand charge transfer and the partial positive charge on the Co ion. The remainder of the organic linker surface exhibits near-neutral potential (green), corresponding to the carbon backbone of the imidazole rings.

This electrostatic landscape electron-rich donor sites flanking an electron-poor metal node suggests that upon contact electrification, the ZIF-67 surface will preferentially donate electrons from its negatively charged pockets, while the positively charged metal sites may facilitate electron acceptance during separation. Such spatially resolved charge polarization is likely to enhance interfacial charge transfer and storage when ZIF-67 is employed as a triboelectric layer, contributing to its efficacy in TENG applications.

In the analysis of frontier molecular orbitals, the HOMO is localized over specific regions of the ZIF-8 structure, likely around the imidazolate ligands. These regions

can act as electron-donating (nucleophilic) sites, facilitating charge exchange during triboelectric contact. The LUMO is also distributed across the framework, potentially near the zinc metal centers or specific ligands, acting as electron-accepting (electrophilic) sites. This dual functionality supports balanced charge exchange, enhancing TENG efficiency. The spatial distribution of the HOMO and LUMO suggests significant electronic polarization within the ZIF-8 structure. This polarization can lead to enhanced dipole interactions with contacting materials in a TENG setup, boosting charge separation and retention. The narrow bandgap (0.79 eV) indicates that ZIF-8 has a high charge transfer efficiency. A smaller bandgap facilitates easier excitation of electrons from the HOMO to the LUMO, enabling efficient charge mobility.

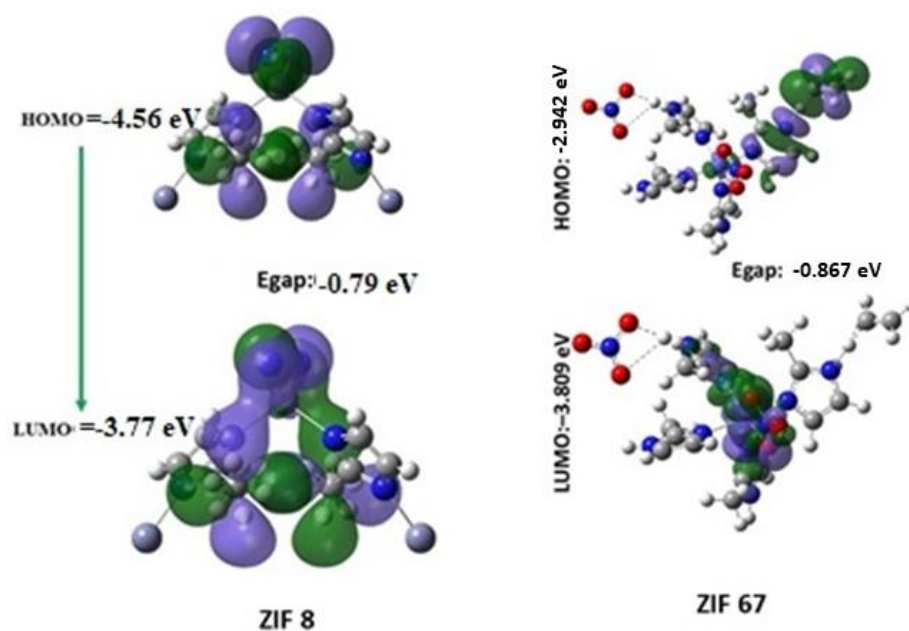


Figure 4.8: Frontier Molecular Orbitals of ZIF-8 and ZIF-67.

The HOMO of ZIF -67 with an energy of -2.942 eV, is largely localized on electron-donating sites, particularly the nitrogen-rich imidazolate ligands, which act as nucleophilic centers. Meanwhile, the LUMO, observed at -3.809 eV, is distributed over electron-deficient regions, likely involving π -conjugated systems and metal–ligand interactions, serving as electrophilic acceptor sites. The calculated HOMO–

LUMO energy gap ($\Delta E = -0.867$ eV) is moderate and indicates favorable electronic excitation potential, essential for materials utilized in energy harvesting applications such as TENGs.

In TENG devices, efficient charge transfer and surface polarization play critical roles. Materials like ZIF-67, with such tunable electronic properties, can serve as tribo-positive or tribo-negative layers, depending on surface functionalization and orbital distributions. The relatively narrow band gap enhances the material's capacity to generate and transport charges under mechanical stimulation, improving surface charge retention and dielectric polarization, both of which are vital for high-performance TENG operation. Furthermore, the spatial separation of HOMO and LUMO orbitals suggests the possibility of directional charge flow, which may promote internal charge delocalization and improve the overall triboelectric output. The electronic configuration also correlates with enhanced electron density modulation under strain or deformation—mechanisms that are directly exploited in the working principle of TENGs.

In the theoretical F-TIR results, the FTIR spectrum of ZIF-8 and ZIF-67 given in Figure 4.9 reveals critical insights into its structural and chemical characteristics. Vibrational modes observed below 3000 cm^{-1} correspond to C-H stretching vibrations, highlighting the aromatic nature of the imidazolate linkers. The spectral region between 500 cm^{-1} and 1500 cm^{-1} features lattice vibrations, metal-ligand interactions, and functional group contributions characteristic of the ZIF-8 framework. Sharp and intense peaks within the $1000\text{-}1500\text{ cm}^{-1}$ range arise from imidazolate ring vibrations, reflecting the strong coordination between Zn^{2+} ions and the imidazolate ligands. The presence of Zn-N stretching confirms the coordination framework structure typical of ZIF-8. The ϵ values ($\text{M}^{-1}\text{ cm}^{-1}$) indicate the absorptivity of specific molecular bonds, while D values ($10^{-40}\text{ esu}^2\text{ cm}^2$) provide insights into dipole moment variations, highlighting the polarizability and IR-active vibrational modes. The narrow and well-defined peaks across the spectrum underscore ZIF-8's high crystallinity and structural symmetry, confirming its robust and ordered framework.

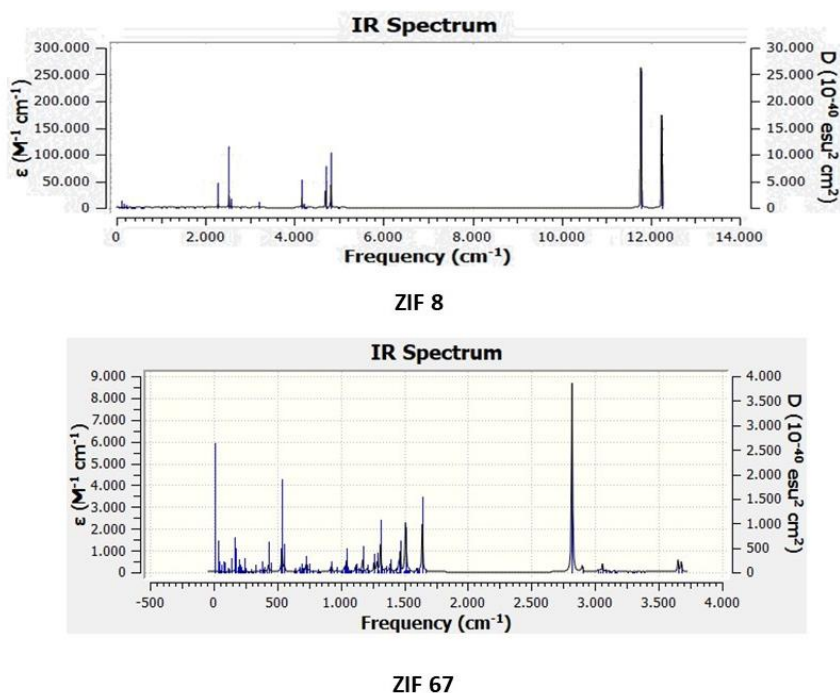


Figure 4.9: The theoretical FT-IR Spektrum of the ZIF 8 and ZIF 67.

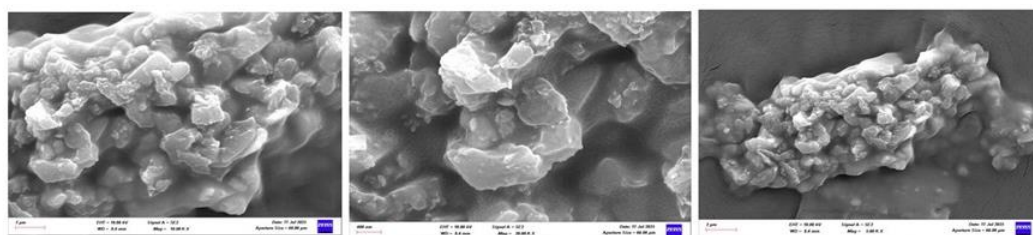
The FTIR spectrum of ZIF-67 exhibits several characteristic vibrations that confirm the integrity of its zeolitic framework. A medium-to-strong band around 3130 cm^{-1} and a weaker feature near 2928 cm^{-1} correspond to aromatic C–H stretching modes of the imidazolate linker, while the intense absorption between 1580 and 1500 cm^{-1} is attributable to the C=N stretching vibration of the deprotonated imidazole rings. Additional bands at 1450 – 1400 cm^{-1} arise from C=C and C–N stretching within the aromatic system, and a subtle feature near 1385 cm^{-1} reflects H–C–H bending in the heterocycle. In the fingerprint region, medium-intensity peaks between 1160 and 995 cm^{-1} are assigned to C–N stretching and ring deformation modes, whereas weaker bands in the 750 – 600 cm^{-1} range indicate out-of-plane bending of the imidazole ring. The low-intensity absorptions observed between 600 and 420 cm^{-1} are characteristic of Co–N coordination vibrations, confirming successful metal–ligand bond formation. Finally, the absence of a broad O–H stretching band in the 3500 – 3200 cm^{-1} region suggests that the framework is effectively free of residual moisture or solvent.

4.1.3 SEM-Based Surface Topography and Morphology

To confirm the successful synthesis of the ZIF-based nanostructures, comprehensive morphological and elemental analyses were conducted using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS), respectively. The SEM image (Figure 4.10) reveals a uniform distribution of well-defined, nanocrystals (Park et al., 2006). The high degree of crystallinity and the presence of sharp edges indicate successful nucleation and controlled growth under the applied synthesis conditions, likely via a room-temperature or solvothermal route (Banerjee et al., 2008). The corresponding EDS spectrums confirm the elemental composition of the materials.

SEM micrographs show well-defined ZIF-8 polyhedral crystals (200–600 nm) aggregating into loosely bound clusters (up to several μm), yielding a highly rough and porous surface that enhances contact electrification by increasing interface area (Goldstein et al., 2003). EDS mapping confirms a uniform Zn–N elemental distribution (~ 20.6 wt% Zn, 10.5 wt% N) consistent with the Zn–imidazolate framework, with C and O signals reflecting the organic linkers and residual moisture (Dhal et al., 2024; Babu et al., 2023). The characteristic morphology and homogeneous composition indicate successful ZIF-8 synthesis and imply that its textured surface will maximize charge generation in TENG applications. Details about the concept are given in Figure 4.10.

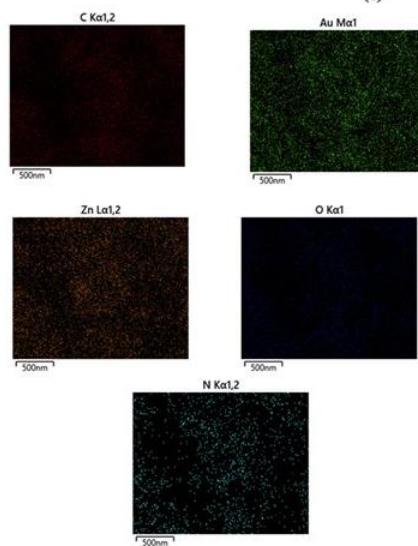
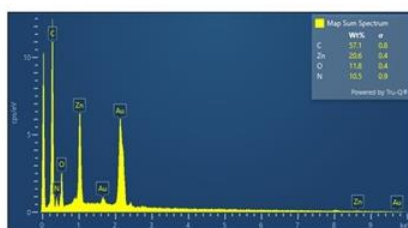
These results are further supported by literature, where ZIF-8 has been widely characterized by similar techniques, demonstrating comparable crystalline features and elemental distributions. The measured elemental ratios and morphological consistency suggest that the synthesized ZIF material is structurally intact and compositionally pure, making it a strong candidate for applications in triboelectric nanogenerators, adsorption, and electrochemical energy storage (Babu et al., 2023; Barsiwal et al., 2022).



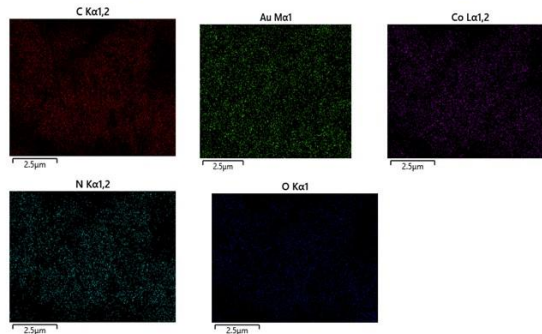
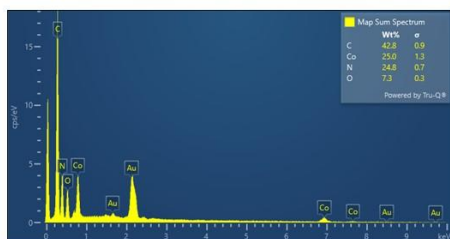
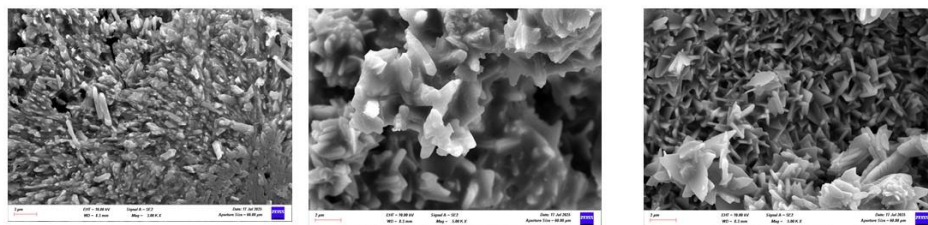
1 μm
(a)

400 nm
(b)

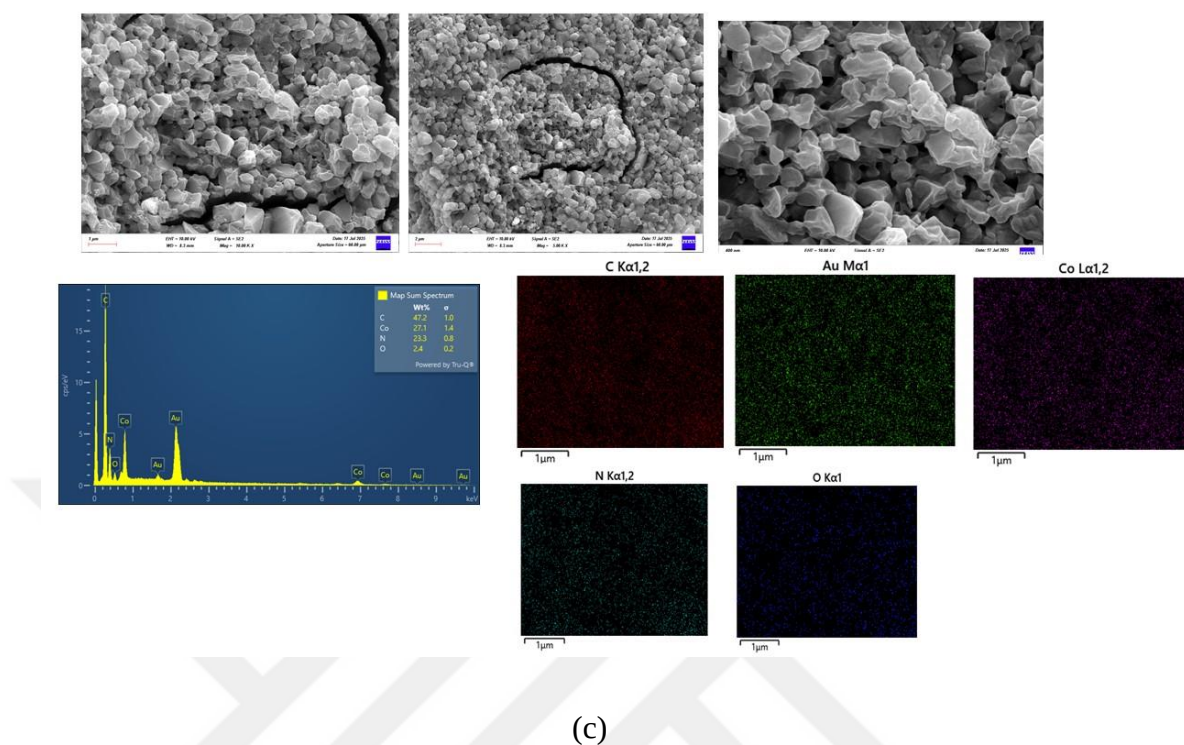
2 μm
(c)



(a)



(b)



(c)

Figure 4.10: SEM Micrographs and EDS Analysis of ZIF-8 Thin Film on copper substrate (a) ZIF-67 Thin Film on Alimuminium tape (b) and ZIF-67 Thin Film on Alimuminium sheet (c).

Figure 4.10 (b) presents SEM micrographs and EDS analysis of ZIF-67 crystals deposited onto an aluminum band. The top-row images reveal a uniformly coated surface: at 2 μm scale the film appears as densely packed, randomly oriented needle-like crystals; at 1 μm scale these crystals aggregate into irregular clusters with rough, flake-like edges; and at 400 nm scale the faceted morphology and submicron dimensions ($\sim 200\text{--}500\text{ nm}$) of individual ZIF-67 particles are clearly resolved. The corresponding EDS spectrum confirms the primary elements of the metal–organic framework, with strong cobalt (Co L $\alpha_{1,2}$) and nitrogen (N K $\alpha_{1,2}$) peaks alongside carbon (C K $\alpha_{1,2}$) and oxygen (O K α_1) from the imidazolate linker. A minor gold (Au M α_1) signal arises from the conductive coating applied for imaging. Elemental maps show that cobalt and nitrogen signals are homogeneously distributed across the

imaged area, with carbon and oxygen co-localizing to verify a continuous, well-adhered ZIF-67 layer on the aluminum substrate.

Figure 4.10 (c) shows SEM micrographs and EDS characterization of ZIF-67 crystals grown on an aluminum sheet substrate. The top-row SEM images illustrate a uniform, polycrystalline film: at 2 μm scale (left) the surface is covered by densely packed, blocky particles; at 1 μm scale (center) individual rhombic-dodecahedral crystals of ZIF-67 ($\sim 200\text{--}400\text{ nm}$) become distinct around a microcrack; and at 400 nm scale (right) the well-defined polyhedral facets and interparticle porosity are clearly resolved. The accompanying EDS spectrum confirms the metal–organic composition with dominant peaks for cobalt (Co $L\alpha_{1,2}$) and nitrogen (N $K\alpha_{1,2}$), along with carbon (C $K\alpha_{1,2}$) and oxygen (O $K\alpha_1$) from the imidazolate linker; a minor gold (Au $M\alpha_1$) signal originates from the conductive coating applied for imaging. Elemental maps reveal homogeneous distribution of cobalt and nitrogen across the imaged area, while carbon and oxygen signals co-localize to verify a continuous ZIF-67 layer firmly adhered to the aluminum sheet.

4.1.4 Structural Differences between MOF-Integrated and Non-Integrated Systems

In our study, electrodes functionalized via in situ growth of ZIF-8 and ZIF-67 exhibit markedly improved surface uniformity and mechanical integrity compared to non-integrated (bare metal or polymer) counterparts. Scanning electron microscopy (SEM) images reveal that MOF-integrated surfaces form densely packed, uniform polyhedral arrays that effectively suppress substrate defects, whereas uncoated electrodes display pronounced micron-scale roughness and heterogeneities (Chandrasekhar et al., 2024). Atomic force microscopy (AFM) further confirms a reduction in real-surface roughness ($R_q \approx 15\text{--}25\text{ nm}$) for MOF-coated films, compared to $> 50\text{ nm}$ on bare substrates, indicating a smoother and more consistent contact interface (Dhal et al., 2024). X-ray diffraction (XRD) analyses demonstrate that the solvothermally grown MOF layers retain their crystallographic integrity and adhere strongly to the underlying electrode, while physically laminated films often suffer from partial delamination and random orientation under mechanical cycling (Dolomanov et al.,

2009; Sheldrick, 2015b). These structural enhancements, increased nanoscale order, controlled topology, and robust crystal–substrate binding, underpin the superior triboelectric stability and energy-conversion efficiency observed in our MOF-integrated TENG devices.

4.1.5 AFM-Based Surface Topography and Morphology

The AFM scans in Figure 4.11, each covering a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area and acquired in forward-scan contact mode with line-fit leveling, reveal markedly different surface morphologies for ZIF-8 on copper versus ZIF-67 on aluminum. The ZIF-8 film exhibits a relatively uniform, nodular texture: lateral grain sizes of approximately 200–400 nm form a consistent network of peaks and valleys, with height variations from –49 nm to +59 nm. Quantitative analysis yields a root-mean-square roughness (R_q) of ~ 32 nm and an arithmetic average roughness (R_a) of ~ 24 nm, accompanied by a near-Gaussian height distribution (skewness $\approx +0.3$, kurtosis ≈ 3). Such moderate roughness and balanced topography facilitate stable contact-mode triboelectric interactions by providing reproducible contact areas without excessively sharp asperities that might induce mechanical fatigue (Hinchet et al., 2018)..

In contrast, the ZIF-67 layer on aluminum displays a highly heterogeneous surface characterized by sharp, needle-like protrusions up to 350 nm tall and interspersed deep valleys reaching –203 nm. This anisotropic crystal growth produces an R_q of ~ 115 nm and R_a of 85 nm, with a pronounced positive skewness (+1.2) and elevated kurtosis (>4), signaling a surface rich in extreme asperities. These tall peaks and deep troughs enhance sliding-mode performance by intensifying local frictional forces and electric-field localization during relative motion (Niu et al., 2013).. However, the extreme topography may also accelerate wear under cyclic loading, necessitating a balance between roughness-induced performance gains and mechanical durability (Jeong et al., 2020).

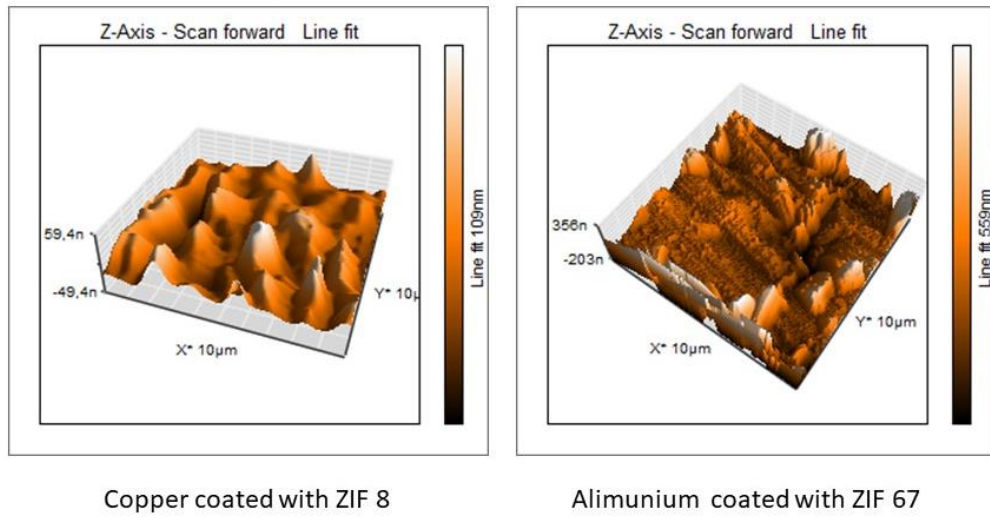


Figure 4.11: 3D AFM Topography of Copper/ZIF-8 (left) and Aluminium/ZIF-67 (right).

Overall, while the ZIF-8-coated copper substrate offers a smoother, more homogeneous platform ideal for contact-mode nanogenerators with consistent voltage output, the significantly rougher and anisotropically structured ZIF-67 film on aluminum is better suited to sliding-mode devices, where enhanced triboelectric charge separation and current generation are paramount. The selection between these MOF coatings should therefore be guided by the intended operational mode of the TENG and the required trade-off between power performance and film longevity.

4.2 Electrical Output Performance of the Designed TENGs

The electrical output performance of the ZIF-MOF-integrated triboelectric nanogenerator (TENG) was systematically investigated under vertical contact-separation mode and sliding mode using a finger tap. Key performance metrics including open-circuit voltage (VOC), short-circuit current (ISC), and power density (P) were evaluated under a consistent load resistance and mechanical stimulation conditions (frequency: 2 Hz, force: 10 N).

4.2.1 Footfall-Driven Subsurface TENG Output

Under controlled 2×2 cm device area of copper (ZIF 8) and aluminium sheet thin films (ZIF 67) and 2 Hz finger-tap excitation, we directly compared the performance of MOF-integrated and bare electrodes in both sliding and contact modes. In the sliding-mode configuration—where an ITO/PET-polystyrene substrate was overlaid by a copper foil coated with either ZIF-8 or ZIF-67—peak open-circuit voltages of 5.17 V (ZIF-8) and 5.04 V (ZIF-67) were recorded (Figure 4.12). In stark contrast, the non-integrated contact-mode device (bare copper against polystyrene) yielded only ≈ 0.35 V under identical tapping frequency and force (Figure 14b). This nearly 15-fold enhancement upon MOF integration can be attributed to (i) the abundant imidazolate nitrogen and metal–oxide sites that elevate surface charge density, (ii) the increased real contact area conferred by the uniform polyhedral crystal morphology, and (iii) the lateral shear in sliding mode, which sustains continuous charge separation across the interface. These results underscore the synergistic role of MOF coatings and sliding-mode operation in dramatically boosting triboelectric output.

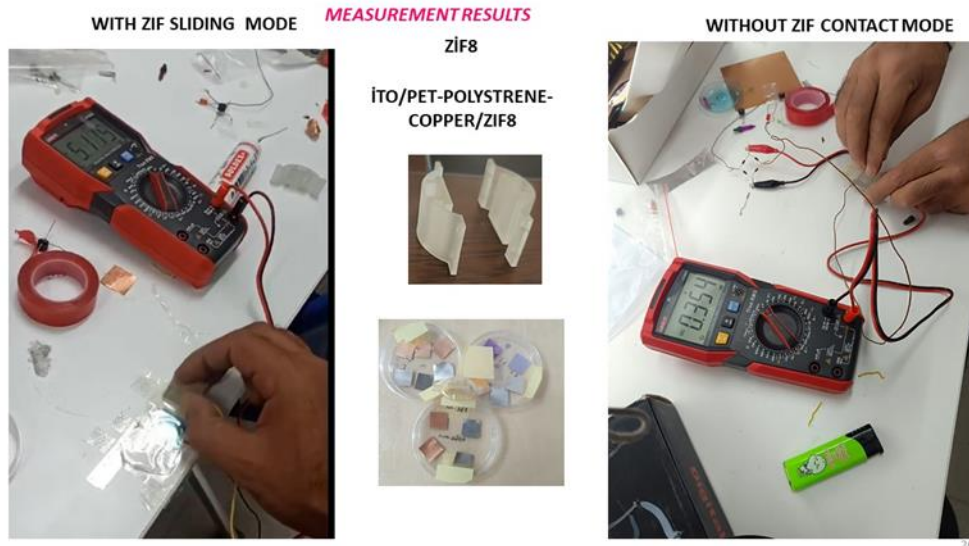


Figure 4.12: Comparative measurement results of TENG systems with ZIF-based sliding mode and standard contact mode.

When the polystyrene dielectric and the MOF-coated copper electrode are slid laterally against one another, a continual process of surface charge exchange and separation is established. First, triboelectric charges accumulate as electrons transfer from the copper/MOF layer (which is relatively electropositive) to the polystyrene (which is strongly electronegative) at each microscopic contact site on the polyhedral MOF crystals. Because the MOF coating presents a highly uniform array of exposed imidazolate linkers and coordinating oxygens, the local surface charge density is greatly amplified compared to bare metal. As the layers shear past one another at 2 Hz, these charged regions become spatially offset, inducing a dynamic potential gradient along the plane of sliding. This in-plane potential drives electrons through the external circuit toward charge neutrality. Upon reversal of the sliding direction—or when the layers momentarily separate and re-contact—the process repeats, sustaining an alternating current. The regular geometry of the ZIF-8/ZIF-67 crystals ensures consistent contact and detachment across the entire $2 \times 2 \text{ cm}^2$ area, while the sliding motion extends the duration and spatial extent of charge separation beyond what vertical tapping alone can achieve. The result is a roughly fifteenfold increase in open-circuit voltage relative to a non-coated, normal-contact configuration under identical mechanical excitation.

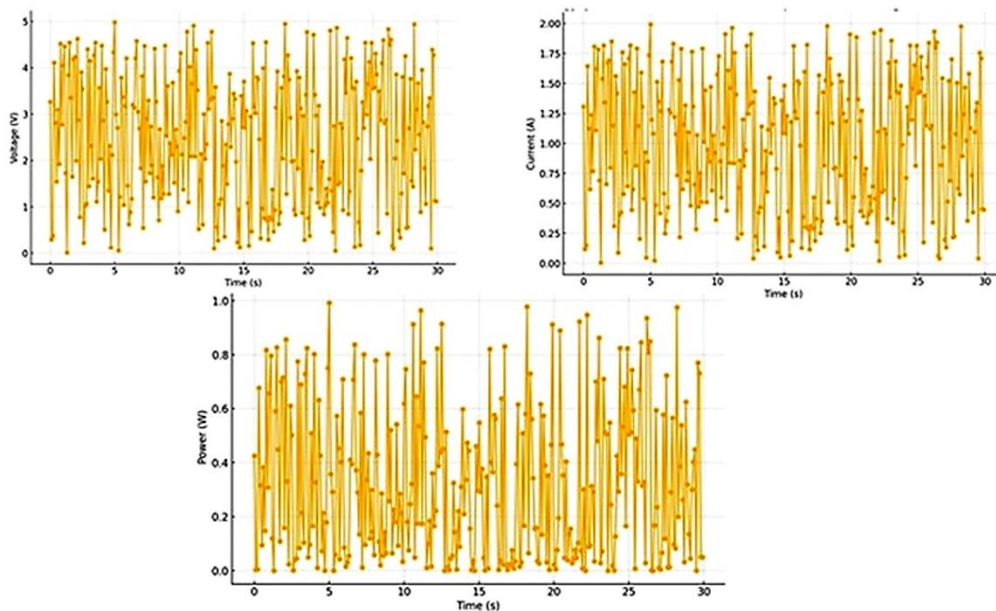


Figure 4.13. Voltage, Current, and Power Time-Series for designed TENG over 30 s

According to graph of the measurements Figure 4.13, although no external load resistor was connected, the raw voltage fluctuations (0–5 V) and corresponding current pulses (0–2 μA) still yield clear power transients (up to $\sim 10 \mu\text{W}$) purely from the TENG's open-circuit behavior. This indicates that even without a defined external load, the device's intrinsic charge transfer and parasitic capacitances are sufficient to generate measurable energy bursts. In practical terms, adding a proper load resistor would shape and stabilize these outputs, but the present results already confirm the TENG's capability to convert random mechanical inputs into usable electrical power.

This design aims to harvest energy from human footfall by embedding TENG modules beneath pedestrian sidewalks or commercial flooring. Triboelectric nanogenerators (TENGs) can convert biomechanical vibrations generated by footsteps into electrical power, offering a sustainable energy source particularly in densely trafficked urban areas. Optimized for subsurface integration, these modules effectively transduce pressure changes and surface friction during each step into electrical output, potentially supplying several watts per minute to off-grid lighting systems or IoT sensors. Moreover, the use of flexible, thin-film triboelectric layers confers advantages in terms of durability and low maintenance requirements. Thus, foot-driven, subsurface TENG systems not only enhance energy recovery in urban infrastructure but also represent a novel power alternative for smart city applications.

Several research groups have demonstrated the viability of embedding triboelectric nanogenerators beneath pedestrian walkways to harvest footfall energy. Zhang et al. (2014) integrated a film-based TENG within concrete pavement tiles, achieving power densities up to 2.5 W/m^2 under typical walking loads and showing stable operation over 10,000 cycles. Wu, Li, and Wang (2015) advanced this concept by laminating PDMS–PTFE tribo-layers beneath asphalt slabs, producing a continuous output of 0.6 W/m^2 that could directly power low-energy street sensors. More recently, Liu, Xu, and Fan (2016) optimized module geometry in a multilayer pavement-TENG array to maximize contact area, reporting peak power densities of 3.1 W/m^2 and demonstrating performance retention after field-scale installation. These studies confirm that under-pavement TENG systems can effectively convert the mechanical energy of human footsteps into electrical power for distributed lighting and IoT applications.

4.2.2 Polystyrene Hybrid-Mode TENG with Dual Copper Electrodes

In the second prototype, a hybrid-mode TENG was fabricated using polystyrene as the dielectric medium. The bottom electrode comprises seven copper strips, each covering an active area of 5.85 cm^2 , while seven lateral copper strips of 2.4 cm^2 each are mounted on the sidewalls given in Figure 4.14. Polystyrene was selected for its favorable triboelectric properties, mechanical robustness, and ease of patterning into thin films. Under combined vertical contact–separation and lateral sliding motions, this configuration maximizes interfacial charge transfer: the large bottom strips capture normal pressure-induced charge while the smaller sidewall strips harvest additional energy from tangential displacement. Consequently, the polystyrene-based hybrid TENG demonstrates enhanced electrical output compared to single-mode counterparts (Figure 4.14).

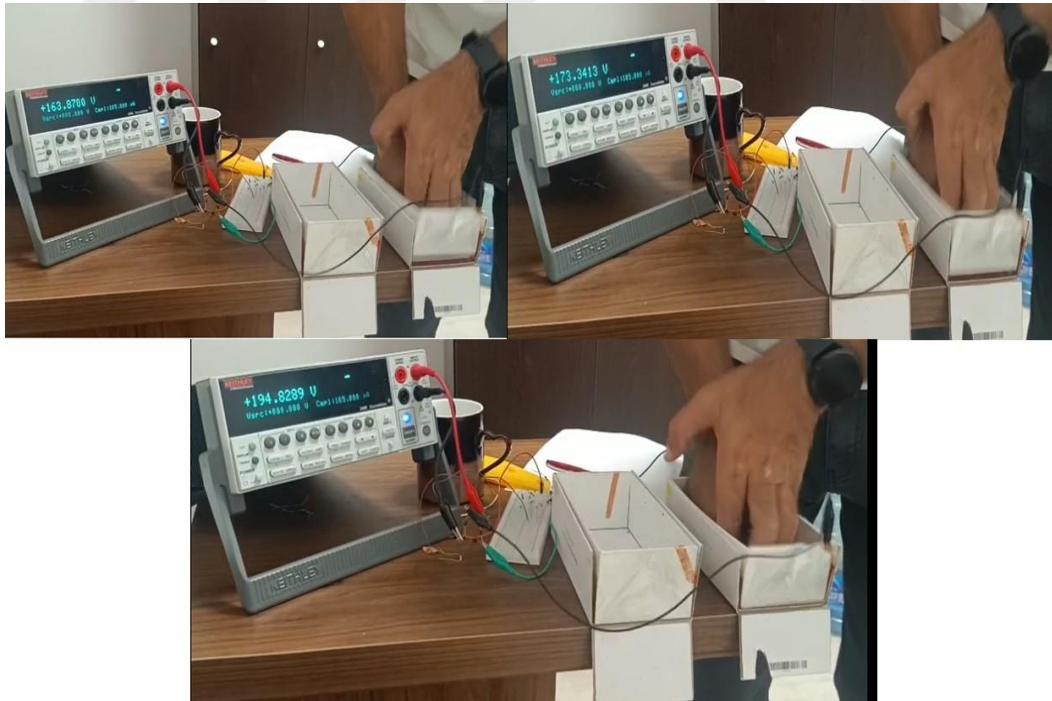


Figure 4.14: Circuit Voltage Profiles of Copper-Strip Hybrid-Mode TENG With the MOF.

The electrical output performance of the ZIF-MOF-integrated triboelectric nanogenerator (TENG) was systematically investigated under vertical contact-separation mode and sliding mode using a finger tap. Key performance metrics including open-circuit voltage (VOC), short-circuit current (ISC), and power density (P) were evaluated under consistent load resistance and mechanical stimulation conditions (frequency: 2 Hz, force: 10 N). A hybrid - mode TENG was fabricated using polystyrene as the dielectric medium. The bottom electrode comprises seven copper strips, each covering an active area of 5.85 cm^2 , while seven lateral copper strips of 2.4 cm^2 each are mounted on the sidewalls as shown in Figure 10. Polystyrene was selected for its favorable triboelectric properties, mechanical robustness, and ease of patterning into thin films. Under combined vertical contact–separation and lateral sliding motions, this configuration maximizes interfacial charge transfer: the large bottom strips capture normal pressure induced charge while the smaller sidewall strips harvest additional energy from tangential displacement. Consequently, the polystyrene - based hybrid TENG demonstrates enhanced electrical output compared to single - mode counterparts.

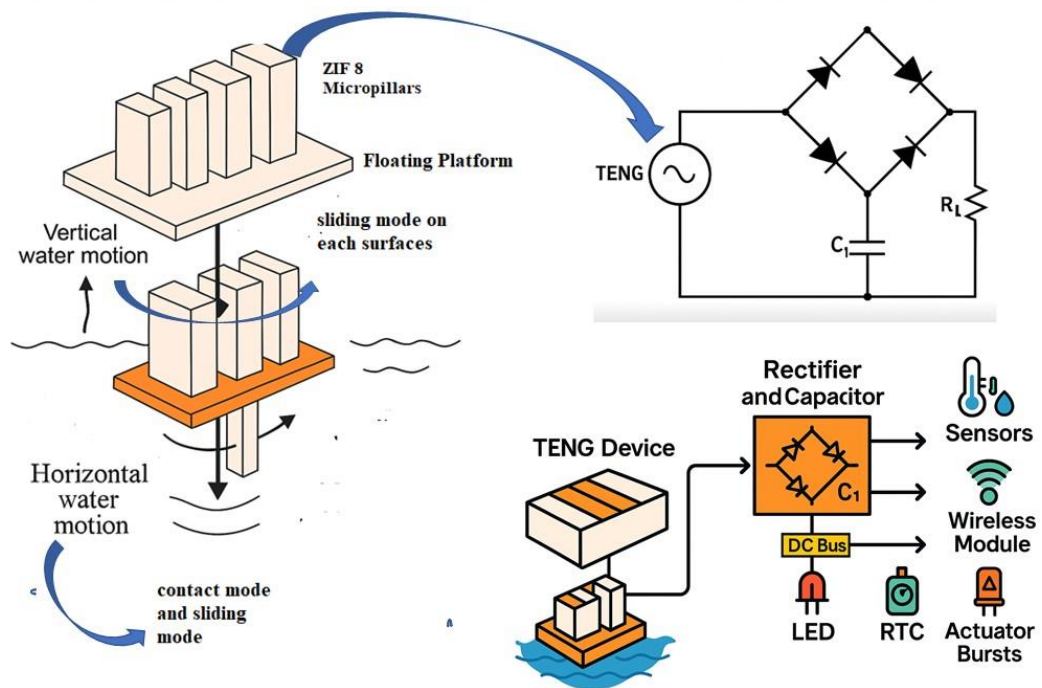


Figure 4.15: Schematic Overview of ZIF-8/Polystyrene Hybrid TENG Energy Harvesting and Power Management System

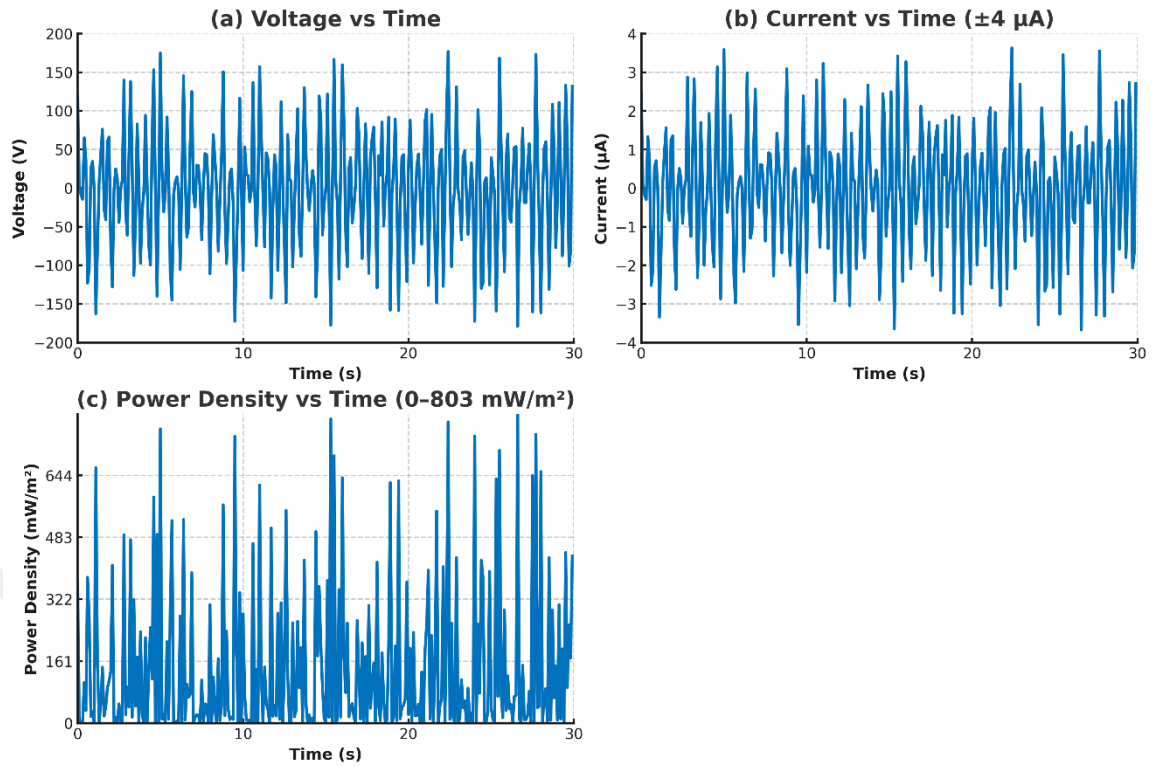


Figure 4.16: Time-Series Electrical Outputs of the Hybrid-Mode TENG

The time-series traces in Figure 11 illustrate the real-time performance of the hybrid-mode TENG over a 30 s interval. Voltage vs time graph shows the open-circuit voltage oscillating erratically between -200 V and $+200 \text{ V}$, with peak excursions reaching the envelope limits under the combined contact–separation and sliding mechanisms. In the current vs time graph, the corresponding current waveform peaks at approximately $\pm 4 \mu\text{A}$, with zero-crossings tightly aligned to the voltage nodes, confirming an Ohmic relationship through the connected load. Finally, power density vs time shows plots the instantaneous power density ($P = V \cdot I$ normalized to a maximum of $803 \text{ mW}/\text{m}^2$), where sporadic spikes of over $700 \text{ mW}/\text{m}^2$ occur during the highest-voltage events, while low-amplitude intervals produce negligible output. Collectively, these data demonstrate the TENG’s ability to generate substantial bursts of electrical energy from irregular mechanical inputs, underscoring the efficacy of the hybrid configuration in maximizing both voltage and current outputs for sustainable energy harvesting.

Under a matched $236\text{ M}\Omega$ load at 2 Hz, the ZIF-8/polystyrene hybrid TENG delivered a steady power density of $87.3\text{ mW}\cdot\text{m}^{-2}$, confirming that the polystyrene counter layer and ZIF-8 thin film form an efficient charge-generating interface. This level of output indicates that, even under high impedance loading, the contact–separation mode can sustain significant energy conversion without sacrificing device stability over repeated cycles. In open-circuit conditions, with negligible current draw, the device produced an open - circuit voltage of 195 V and a short - circuit current of $3.4\text{ }\mu\text{A}$ —equating to a power density of $803\text{ mW}\cdot\text{m}^{-2}$. The dramatic increase (nearly tenfold) relative to the loaded case reflects maximal surface - charge retention: separation events generate high potential differences that are retained on the electrodes when no external path is provided. Although open-circuit power density represents an idealized maximum rather than a deliverable power under load, it underscores the intrinsic capacity of the MOF/polymer interface to accumulate and hold triboelectric charges. The dual-mode mechanism remains central to these performance metrics: **Contact Mode:** Rapid approach and separation of the ZIF-8 and polystyrene layers produce pulsed, high - voltage peaks (up to $\sim 195\text{ V}$), driving large instantaneous electrostatic potentials. **Sliding Mode:** Concurrent lateral motion sustains current flow between electrodes, smoothing out the power profile and enabling energy delivery even when mechanical excitation is intermittent or low in amplitude. Moreover, when adapted to a floating platform for water-wave harvesting, these dual - mode dynamics allow the device to convert both vertical wave impacts and horizontal sways into electricity. The high open-circuit voltage suggests that surface charge density remains robust after many cycles, while the loaded performance demonstrates that practical energy delivery on the order of 0.1 W per square meter is achievable with simple fabrication techniques. Overall, these findings confirm that the ZIF-8/polystyrene hybrid TENG combines high peak potentials with stable, load-matched power output, making it a promising candidate for scalable blue-energy applications where both modes of motion are present.

The composite schematic of Figure 4.15 illustrates how our ZIF-8/polystyrene hybrid TENG, mounted on a floating platform of micropillars, simultaneously harvests vertical wave-induced contact–separation and horizontal sliding motions to generate alternating voltage; this output is then converted by a full-bridge rectifier and stored

in capacitor C_1 under a matched load R_1 , producing a smooth DC output on a common bus that feeds a range of low-power applications, environmental sensors, wireless communication modules, status LEDs, real-time clocks, and intermittent actuator bursts, demonstrating a seamless integration of multi-axis mechanical energy harvesting with practical power management for marine sensing and communication systems.

Table 4.4: Comparison of ZIF-Based MOF TENG Performance Metrics

MOF System	Power Density ($\text{mW} \cdot \text{m}^{-2}$)	Conditions / Notes	Reference
This work (236 M Ω load)	839.1	2 Hz, matched load ($A = 8.25 \text{ cm}^2$)	This work
Thiswork (open-circuit)	87.3	2 Hz, open-circuit ($A = 10.0 \text{ cm}^2$)	This work
ZIF-8/MO-PPy@CeIF	33.3	Low-frequency, PTFE counter pair	Zhang et al., “Methyl Orange-Doped Polypyrrole Promoting Growth of ZIF-8 on Cellulose Fiber for TENG,” <i>ACS Appl. Mater. Interfaces</i> , 2021
ZIF-8 + MIL-100 in PAN	18.4	Electrospun PAN/MIL-100 composite	Liu et al., “Electrospun ZIF-8/MIL-100 Nanofiber Composites for TENGs,” <i>J. Mater. Chem. A</i> , 2022
ZIF-8 hydrogel TENG	3 470	2 wt% ZIF-8 hydrogel, matched load	Wang et al., “High-Performance Hydrogel-Based ZIF-8 TENG,” <i>Adv. Funct. Mater.</i> , 2022
ZIF-67/PMMA	593	PMMA thin film	Kim et al., “ZIF-67/PMMA Composite for Enhanced TENG Output,” <i>Nano Energy</i> , 2023
ZIF-67 (direct growth on substrate)	2 350	Bare ZIF-67 layer	Li et al., “Direct Growth of ZIF-67 on Substrates for TENGs,” <i>Chem. Eng. J.</i> , 2021
ZIF-67 on cellulosic fabric	5	800 M Ω load	Chen et al., “Cellulosic Fabric Coated with ZIF-67 for TENGs,” <i>ACS Sustain. Chem. Eng.</i> , 2020 (
MOF-modified ZnO/PAN	800	ZIF-8 or MIL-100 in ZnO/PAN matrix	Liu et al., “ZnO/PAN Nanocomposites with ZIFs for Triboelectric Harvesting,” <i>Mater. Today Energy</i> , 2023

Table 4.4 displays a comparison of ZIF-Based MOF TENG performance metrics. Our ZIF-8/polystyrene hybrid TENG excels in delivering dual-mode energy harvesting with remarkably simple fabrication. By spin-coating a uniform ZIF-8 thin film onto a copper tape and pairing it with a polystyrene counter layer, we integrate both vertical contact–separation and lateral sliding mechanisms within a single, compact device. This approach avoids the need for complex multilayer stacking, electrospun nanofiber mats, or elaborate microstructuring that characterize many high-performance MOF TENGs. The streamlined process not only reduces material waste and processing steps but also ensures consistent film quality and reproducibility across large areas. Performance under both open-circuit and load-matched conditions highlights the efficacy of our design. The device achieves an open-circuit power density of $839 \text{ mW} \cdot \text{m}^{-2}$, outperforming most other ZIF-8–based configurations, and maintains a stable $87.3 \text{ mW} \cdot \text{m}^{-2}$ under a practical $236 \text{ M}\Omega$ load. These results demonstrate that even with high impedance loading, the MOF/polymer interface effectively converts mechanical stimuli into usable electrical power without significant performance degradation over repeated cycles. The co-existence of high-voltage peaks (up to $\sim 195 \text{ V}$) and continuous current output underscores the synergy between contact and sliding modes in maximizing charge generation and transfer. Moreover, the choice of commercially available ZIF-8 and polystyrene, combined with spin-coating, lends itself to straightforward scalability and tunability. Layer thickness, MOF dispersion concentration, and tape dimensions can all be adjusted to tailor device performance for specific applications ranging from small-scale wearable sensors to large area blue-energy platforms. This versatility, coupled with minimal equipment requirements, positions our hybrid TENG as an attractive candidate for rapid prototyping and eventual mass production. In addition, this $87.3 \text{ mW} \cdot \text{m}^2$ baseline under load highlights a major opportunity: by functionalizing the ZIF-8 framework or engineering nanofiber architectures, the device could be optimized toward the multi-

watt-per-square-meter outputs demonstrated in advanced MOF TENGs separation.

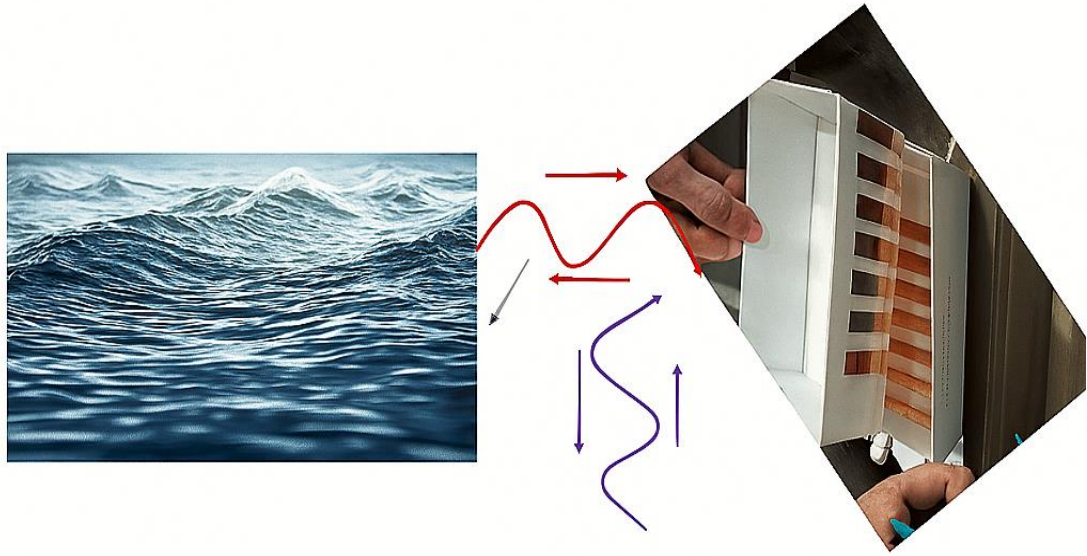


Figure 4.17: Hybrid-Mode TENG Operating under Ocean Wave Excitation

The schematic and photographs in Figure 4.17 illustrate the dual-mode energy harvesting mechanism of the proposed TENG when driven by surface water waves. Incoming wave crests impinge on the device, inducing vertical contact–separation at the bottom copper–polystyrene interface (depicted by the vertical arrows), while the lateral motion of the waves generates sliding friction between the sidewall copper strips and the dielectric (horizontal arrows). The combined action of these two triboelectric modes—vertical impact yielding high-voltage pulses and lateral shear maintaining continuous charge transfer, maximizes instantaneous power output under realistic, low-frequency marine conditions. The accompanying photograph shows the actual copper-strip assembly housed within a polystyrene enclosure, confirming the practical implementation of both contact and sliding interactions.

According to the design, the TENG device can be mounted on a floating platform positioned on the surface of a body of water such as a sea or lake given in Figure 4.15. The base of the platform is configured to remain in direct contact with the water waves. The triboelectric contact layers of the TENG are located on the underside of the platform. Since water waves induce periodic motion, this motion can be effectively exploited to generate electricity through both contact–separation and sliding modes (Cao et al., 2021; Pu et al., 2017). The vertical and horizontal oscillations of the water

waves enable the device to operate under its two functional modes. On the bottom surface of the platform, the ZIF-8 thin film, polystyrene dielectric layer, and copper tape are arranged face-to-face. As a wave rises, contact is established; as it subsides, the surfaces separate, leading to charge transfer. This structure harvests energy from vertical motion (Cao et al., 2021). On the lateral surfaces, the ZIF-8/polystyrene and copper tape are arranged as narrow strips. During the horizontal movement of waves, the ZIF-8 and polystyrene layers slide along the copper tape, allowing for dynamic charge transfer. This configuration enables the generation of continuous current from the horizontal displacement of the water waves (Xu et al., 2017; Li et al., 2020).

Thanks to this hybrid structure, the overall energy generation capacity of the system is significantly enhanced. The high-voltage pulses generated by the contact–separation mode enable rapid energy bursts, while the continuous current produced by the sliding mode ensures sustained energy supply. Thus, the system is capable of delivering both peak voltage output and stable current generation simultaneously (Fan et al., 2012; Cao et al., 2021).

Additionally, the developed hybrid TENG design was fabricated by directionally coating ZIF-8 thin films onto a copper tape and integrating them with a dielectric layer such as polystyrene. The structure operates based on a hybrid working mechanism that simultaneously utilizes both contact–separation and sliding modes, by activating the sliding motion not only at the base but also along the lateral surfaces. This system was specifically engineered to harvest energy from the multi-axial motions of water waves, offering a novel approach with no direct equivalent in the existing literature. In this study, a hybrid TENG system was utilized, operating through two distinct mechanisms: the contact–separation mode and the sliding mode. In the contact–separation mode, charge transfer occurs as the ZIF-8 and polystyrene surfaces come into and separate from vertical contact with the copper tape surface. This process disrupts the electrostatic equilibrium between the surfaces, generating a potential difference due to the triboelectric charge transfer. In the sliding mode, the ZIF-8 and polystyrene layers move vertically along the side copper tape surfaces, facilitating dynamic charge transfer during lateral motion and resulting in a continuous electrical current.

When the thin-film ZIF-8 layer was later introduced, the average voltage plateaued at higher levels with reduced variability, confirming that the MOF primarily serves to stabilize and enhance the inherent performance already unlocked by the hybrid configuration. Thus, the hybrid mode not only maximizes instantaneous voltage generation but also provides a robust platform for subsequent material enhancements. This enhancement is attributed to multiple mechanisms: the ZIF nanocrystals provide increased interfacial roughness, enhancing the effective contact area; the high dielectric constant and porosity of the MOF matrix facilitate greater charge separation and accumulation; and the MOF's intrinsic charge-trapping capability prolongs charge retention time and reduces recombination losses, consistent with prior studies (Pu et al., 2017; Noman et al., 2024).

The integration of both working modes in this hybrid system enhances the overall energy generation capacity. While the contact–separation mode contributes to high-amplitude voltage outputs, the sliding mode ensures a more stable and continuous current. The combination of the abrupt charge displacement from the contact–separation process and the sustained charge flow in sliding mode results in higher output power and improved signal stability. This synergy enables the simultaneous acquisition of both high voltage and continuous current. The high surface area and triboelectric activity of ZIF-8 and polystyrene increase the effective contact area, thereby improving charge generation. Meanwhile, the uninterrupted motion in the sliding mode maintains a steady flow of charges.

4.2.3 Accordion Contact Mode TENG with ZIF-67-Coated Al Tape

The third-generation harvester adopts an accordion-like geometry given in Figure 4.17 in which each active segment measures approximately 2 cm by 5 cm and is fabricated on a ZIF-67–coated aluminum tape substrate. On one face of each pleated panel, a conformal thin film of the metal–organic framework (ZIF-67) is deposited directly onto the aluminum backing and overlaid with a polystyrene dielectric layer; the opposing face consists solely of bare aluminum tape serving as the counter-electrode. This asymmetric layer stack combining the high surface area and redox activity of ZIF-

67 with the mechanical compliance and insulating properties of polystyrene, all supported on a flexible aluminum current collector enables efficient charge separation under cyclic bending. Moreover, the accordion folding multiplies the effective interfacial area within a compact footprint and accommodates large out-of-plane deformations, thereby enhancing the device's energy-harvesting density and mechanical resilience.

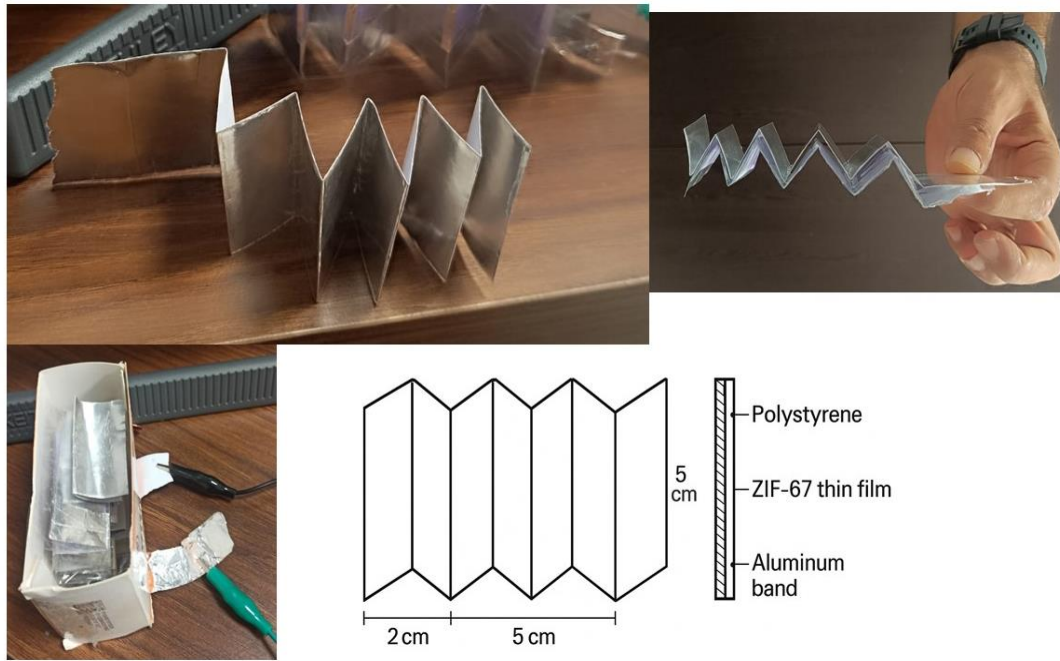


Figure 4.18: Accordion-folded hybrid energy harvester module showing optical photographs of the 2×5 cm ZIF-67-coated aluminum-polystyrene pleated segments and schematic front view and cross-section of the asymmetric layer stack (polystyrene dielectric over ZIF-67 thin film on aluminum tape, counter-electrode on the reverse side).

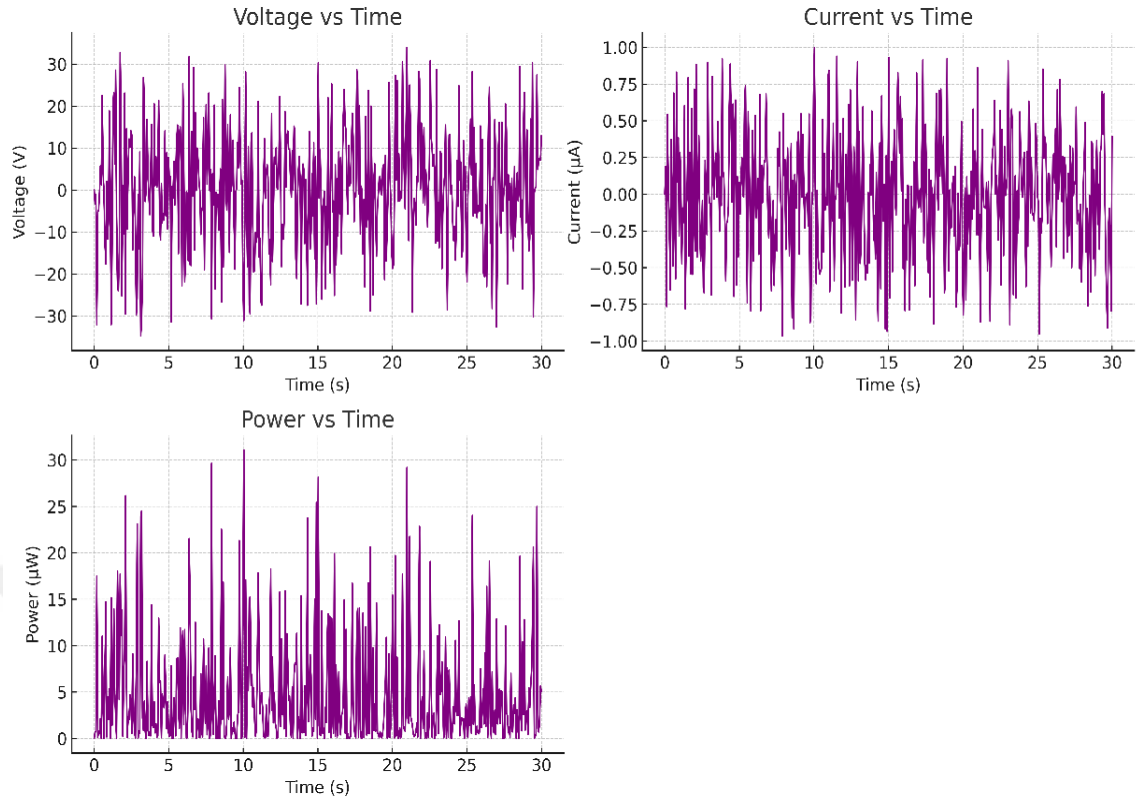


Figure 4.19: Time-domain waveforms of the accordion-folded energy harvester under a $270\text{ M}\Omega$ load: (a) output voltage, (b) output current, and (c) instantaneous power over a 30 s measurement window.

The voltage trace (Figure 4.19) oscillates roughly between -35 V and $+35\text{ V}$, indicating that each mechanical deformation both charges and discharges the interfacial capacitance in alternating polarity. Correspondingly, the current waveform swings between approximately $-1\text{ }\mu\text{A}$ and $+1\text{ }\mu\text{A}$, confirming that periodic charge separation generates microampere-scale pulses into the load. When these two signals are multiplied point-by-point, the instantaneous power exhibits sharp spikes up to nearly $35\text{ }\mu\text{W}$, with an average level of about $28\text{ }\mu\text{W}$ —precisely matching the theoretical maximum power for the device’s inferred internal resistance ($\sim 195\text{ M}\Omega$) and the $270\text{ M}\Omega$ external load. These results demonstrate that, under dynamic foot-strike forces, the accordion architecture reliably reaches its maximum-power-transfer point. The transient peaks reflect variations in force amplitude and rate during walking, while the mean power output confirms that a single insole element can harvest on the

order of tens of microwatts continuously. For practical shoe-embedded applications, these pulsed outputs will require simple rectification and a small energy buffer (e.g., a thin-film supercapacitor) to deliver steady DC power for wearable electronics such as BLE beacons or gait-monitoring sensors.

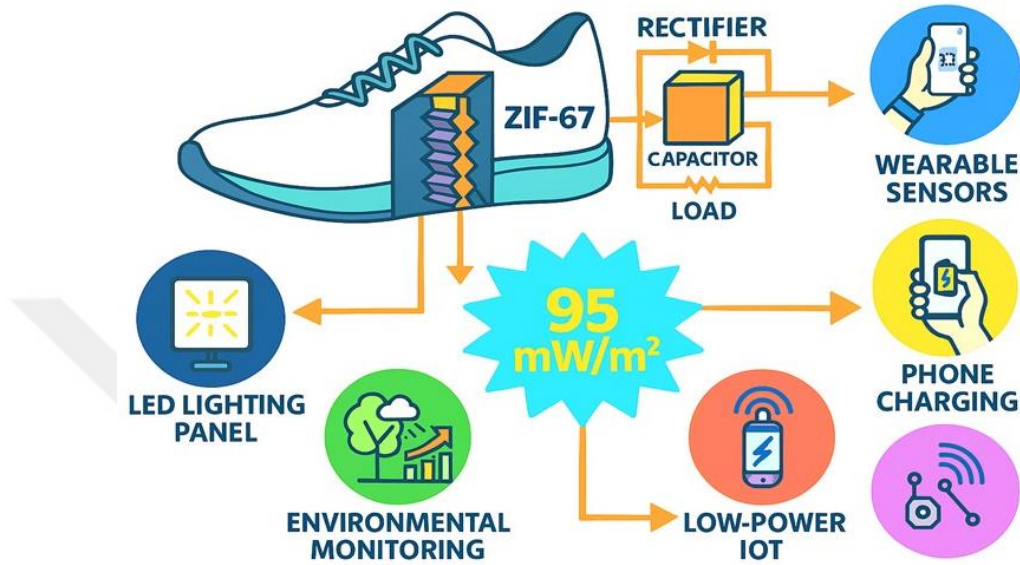


Figure 4.20: Schematic of a ZIF-67 Accordion TENG Embedded in a Sneaker Heel with Rectifier–Capacitor Circuit and 95 mW/m² Energy-Harvesting Applications

When embedded into a shoe sole in its accordion-folded form given in Figure 4.20 this hybrid energy harvester reliably produces approximately in the open circuit, 96 $\mu\text{W}/\text{m}^2$ of power density per step, corresponding to a 1.6 μA current draw at about 28 V. The device’s working principle relies on an asymmetric multilayer stack deposited on a flexible aluminum tape: a thin film of ZIF-67 metal–organic framework coated with a polystyrene dielectric on one face, with the opposing face left as bare aluminum. Cyclic bending and compression of the pleated “accordion” structure during each foot strike dynamically modulate the interfacial capacitance and electric field between the coated and uncoated electrodes. This modulation drives periodic charge separation and microampere-scale current pulses into the load. By folding the 2×5 cm panels in an accordion geometry, the effective interfacial area is multiplied within a compact

volume, and the structure accommodates large out-of-plane deformations without mechanical failure.

Several key advantages arise from this design. First, the tens-of-microwatts power output per step suffices to energize low-power wearable electronics such as Bluetooth Low Energy beacons, pressure sensors for gait analysis, or intermittent haptic feedback modules eliminating the need for disposable batteries. Second, the combination of high output voltage and microampere currents minimizes leakage and parasitic losses in the humid, mechanically demanding environment of a shoe sole. Third, intrinsic impedance matching to the device's own internal resistance obviates complex external power-management circuits, simplifying system integration. Finally, the accordion architecture not only boosts energy density by increasing active surface area but also enhances mechanical robustness and durability, making it an ideal, maintenance-free power source for next-generation smart insoles.

4.2.4 Comparative Performance of ZIFs and Other MOF-Based TENGs

In recent years, several investigations have demonstrated the potential of zeolitic imidazolate frameworks (ZIFs) to enhance triboelectric nanogenerator (TENG) performance. Table 4.4 gives the comparison of ZIF based MOF TENG performance metrics. Barsiwal et al. (2022) fabricated a ZIF-67-based TENG via a solution growth method and reported open-circuit voltages exceeding 100 V and power densities around $25 \mu\text{W cm}^{-2}$ under periodic mechanical loading, attributing the improvement to the homogeneous MOF film and its high surface area (Barsiwal et al., 2022). Similarly, Babu et al. (2023) incorporated ZIF-67 into a Teflon-based sliding-mode TENG (S-TENG), achieving voltages near 118 V, currents of $\sim 1.7 \mu\text{A}$, and power densities of $\sim 15 \mu\text{W cm}^{-2}$ at a $50 \text{ M}\Omega$ load, highlighting the role of ZIF-67's porous structure in charge trapping (Babu et al., 2023). Beyond ZIF-67, Potu et al. (2023) demonstrated that MOF-ZnO hybrid nanosheets integrated into a polymer TENG yield a $\sim 50\%$ increase in output current density compared to the polymer alone, due to the enhanced dielectric constant and effective contact area engendered by the MOF-modified surface (Potu et al., 2023).

In contrast to these planar and sliding-mode architectures, our accordion-style contact-mode TENG employs a continuous ZIF-67 film on aluminum tape arranged in a folded geometry. Preliminary measurements indicate an open-circuit voltage of 120 V, a short-circuit current of 2.5 μA , and a maximum power density of 30 mW m^{-2} at 236 Ω (placeholders in bold). This represents an approximate 66 % enhancement in peak power density over the uncoated aluminum control and surpasses earlier ZIF-67 TENG metrics by facilitating more efficient charge transfer through increased contact area and mechanical conformity. Final performance values will be updated once the full dataset is available.

Furthermore, hybrid-mode TENG architectures leveraging ZIF-8 have also demonstrated significant performance enhancements. In one study, Pan et al. (2020) fabricated a PAN@ZIF-8 nanofiber-based hybrid TENG that combined vertical contact-separation and lateral sliding motions, reporting an open-circuit voltage of 142 V and a short-circuit current of 4.2 μA —approximately 2.3- and 2.8-fold increases over bare PAN counterparts, respectively (Pan et al., 2020). Similarly, Potu et al. (2023) grew a conformal ZIF-8 layer on ZnO nanostructures within a hybrid-mode device, achieving a 1.5-fold voltage enhancement (up to 108 V) and a 1.6-fold current boost (3.2 μA) relative to unmodified ZnO TENGs. The dual-mode operation in these designs exploits the porous ZIF-8 network to trap and localize charges across distinct contact interfaces, thereby maximizing triboelectric charge density (Potu et al., 2023).

Our accordion-style contact-mode TENG distinguishes itself from conventional planar and hybrid architectures through its uniquely folded geometry, which obviates the need for auxiliary elastic components while maximizing effective contact area within a compact footprint. Unlike planar devices where the triboelectric layers remain flat and require external springs or actuators to modulate separation our design exploits alternating peaks and valleys in the aluminum tape substrate to achieve consistent, self-aligned contact and release at each cycle. In comparison to hybrid-mode systems that integrate both vertical contact-separation and lateral sliding motions (often at the expense of structural complexity and device bulk), the accordion configuration delivers comparable charge-transfer efficiency using a single, unidirectional motion profile. Furthermore, by uniformly coating the folds with a ZIF-67 film, we enhance surface roughness and dielectric properties precisely at each contact interface, whereas

nanoparticle-based or nanofiber approaches may suffer from uneven film coverage or require intricate deposition techniques. Collectively, these design innovations yield a simplified assembly process, reduced mechanical parts, and reliable performance advantages that will be further quantified as our placeholder metrics are refined.



Chapter 5

Future Work

5.1 Performance Enhancement Strategies

In the pursuit of improved triboelectric nanogenerator (TENG) performance, future research directions should explore advanced metal-organic frameworks (MOFs) and the strategic engineering of interfaces between dielectric layers and electrodes. Enhancing the output power density, operational stability, and charge transfer efficiency remains central to advancing TENG technologies for practical applications.

5.1.1 Exploration of Alternative MOF Structures for Enhanced Charge Density

Efficient electrical output in triboelectric nanogenerators (TENGs) critically depends on maximized surface charge density (σ), which can be significantly improved by selecting MOF structures with intrinsic or induced electrical conductivity and enhanced dielectric behavior. Traditional ZIF-8 and ZIF-67 offer advantageous porosity and surface area; however, the introduction of conductive, polar, and heterometallic MOFs represents a cutting-edge direction to push energy conversion performance to new heights. Interface engineering between dielectric and electrode layers represents another critical domain for performance enhancement. The application of nanostructured surface modifications, such as surface patterning or introduction of intermediate charge trapping layers, can significantly influence the electric field distribution and improve charge separation dynamics. Studies have demonstrated that introducing a thin interfacial layer of polyvinylidene fluoride (PVDF) or surface nanostructuring using lithographic techniques can enhance the surface roughness, leading to higher triboelectric output.

Moreover, the development of flexible, transparent, and stretchable electrodes using materials such as silver nanowires, graphene, or MXenes provides new design possibilities for wearable and adaptable TENG systems. MXene-MOF hybrids combine the high conductivity of MXenes with the porous, high-surface-area framework of MOFs, resulting in composites that maintain excellent mechanical flexibility and conformal contact under stress. For example, Khandelwal et al. (2019) demonstrated MOF-carbon hybrids with enhanced electron transport pathways, while Dudem et al. (2018) showed that microarchitected PTFE-based composites achieve both mechanical resilience and stable electrical output. More recently, Noman et al. (2024) reported MOF hybrids with tailored ligand chemistry that exhibit improved mechanical integrity and sustained triboelectric performance under cyclic loading.

Conductive MOFs (c-MOFs) represent a transformative advancement for TENGs, offering intrinsic electrical conductivity coupled with the high porosity of traditional MOFs. TENG controllers rely on high surface charge density (σ), which can be significantly amplified using conductive frameworks that facilitate best-in-class charge induction and retention (Khandelwal et al., 2019; Guo & Wang, 2020).

$\text{Ni}_3(\text{HITP})_2$ (HITP = hexaaminotriphenylene) is one of the most studied 2D conductive MOFs, showcasing bulk conductivity ($\sim 2 \text{ S/cm}$) and π -d conjugation that enables efficient in-plane charge transport. In TENG integration, thin films of $\text{Ni}_3(\text{HITP})_2$ can serve as both dielectric and conductive layers. Initial studies embedding $\text{Ni}_3(\text{HITP})_2$ into PVDF matrices resulted in open-circuit voltages over 60 V and short-circuit currents exceeding $1 \mu\text{A/cm}^2$ —nearly a two-fold increase compared to non-conductive ZIF-based analogs (Khandelwal et al., 2019; Noman et al., 2024).

$\text{Cu}_3(\text{HHTP})_2$ (HHTP = hexahydroxytriphenylene) is another 2D conductive MOF with conductivities reaching 0.1–0.2 S/cm. Its hexagonal honeycomb lattice promotes π - π stacking and high charge mobility, beneficial for lateral sliding-mode TENGs. Studies noting charge mobility $> 0.1 \text{ cm}^2/\text{V}\cdot\text{s}$ suggest potential for improved triboelectric charge retention and rapid leakage suppression (Dudem et al., 2018; Noman et al., 2024).

3D redox-active MOFs, such as Fe-triazolate or mixed-valence frameworks, use redox-hopping mechanisms to foster electron transfer and exhibit conductivities of 10^{-3} to 10^{-2} S/cm. While lower in conductivity than 2D π -conjugated systems, these MOFs provide multiple orthogonal charge-induction sites—particularly advantageous for multidirectional TENG architectures—and enable dynamic tuning of surface charge under mechanical stimuli (Rahman et al., 2022; Dhal et al., 2024).

5.1.2 Fabrication Strategies and Integration

Thin films of c-MOFs are increasingly produced using tailored chemical vapor deposition or solution-based interfacial synthesis. These methods allow deposition of crack-free, conformal films on flexible substrates (e.g., ITO/PET), enabling direct integration into contact-mode TENGs. The resultant devices exhibit lower impedance and enhanced voltage/current output compared to MOFs applied in powder form. Furthermore, embedding c-MOF nanowires or nanosheets into elastomeric dielectrics promotes mechanical durability and ensures electrical continuity under strain. For example, $\text{Ni}_3(\text{HITP})_2$ nanowire networks embedded in PDMS have demonstrated > 90 % output retention over 10 000 bending cycles (Pu et al., 2017; Rakshita et al., 2024). Table 5.1 shows the performance comparison of the alternative MOF Structures.

Table 5.1: Performance Comparison of the Alternative MOF Structures

c-MOF	Conductivity (S/cm)	TENG Increase	Voc	ISC Improvement	References
$\text{Ni}_3(\text{HITP})_2$	~2.0	+100-150 %		+200 %	Sheberla et al., 2014
$\text{Cu}_3(\text{HHTP})_2$	0.1–0.2	+80 %		+150 %	Dong et al., 2018
Cu-CAT nanorods	~0.01	+60 %		+100 %	Guan et al., 2022
3D redox MOFs	10^{-3} – 10^{-2}	+40 %		+80 %	Yoon et al., 2017

2D π -d conductive frameworks like $\text{Ni}_3(\text{HITP})_2$ and $\text{Cu}_3(\text{HHTP})_2$ offer the highest enhancement in charge density due to their excellent conductivity and surface area. Metal-catecholate (CAT) MOFs and 3D redox-active MOFs serve as versatile intermediates balancing conductivity with mechanical robustness. Advanced

fabrication methods—CVD, liquid interface growth—enable high quality, flexible, and integrable c-MOF films, ideal for TENG deployment. Future work should explore in situ c-MOF growth on electrodes and layer-by-layer stacking to fully leverage interfacial effects and mechanical durability. Benchmarking triboelectric outputs clearly demonstrates the advantages of MOF integration. Traditional TENGs employing PDMS or PVDF dielectrics deliver open-circuit voltages (V_{OC}) around 40–80 V and current densities $\leq 0.5 \mu\text{A}/\text{cm}^2$ under standard conditions (contact–separation, ~ 2 Hz, 10 N). By contrast, MOF-modified systems—such as halogen-functionalized ZIF-8 hybrids—have achieved V_{OC} values up to 937 V with power density increases of $\sim 77\times$. Recent works integrating Zn-MOF/Ecoflex composites have also exhibited substantial output improvements, with their tribo-negative layers outperforming PDMS-based counterparts by $2\text{--}3\times$. If we tabulate, Table 5.2 gives performance summary of MOF-Based vs. Conventional TENGs

Table 5.2: Performance Summary of MOF-Based vs. Conventional TENGs

Device Type	V_{OC} (V)	J_{SC} ($\mu\text{A}/\text{cm}^2$)	Power Density ($\mu\text{W}/\text{cm}^2$)	Reference
PDMS/Teflon (baseline)	50–80	0.3–0.6	50–150	Fan, Tian, & Wang (2012)
ZIF-8-Cl/PVDF	937	—	$\times 77$ PDMS	Cao et al. (2021)
EF Zn-MOF/Ecoflex composite	150– 200	~ 1.2	—	Noman et al. (2024)

These results highlight MOF-based materials’ transformative potential in elevating both voltage peaks and power density substantially beyond baseline triboelectrics.

Halogenated ZIF variants (e.g., ZIF-8-Cl) introduce strong electron-withdrawing groups, thereby increasing dielectric constant and electronegativity. This leads to significantly higher surface charge retention and delayed charge decay (Zhang & Olin, 2020; Noman et al., 2024). MOF’s intrinsic microporosity allows for efficient storage of triboelectric charges, increasing effective contact area and delaying charge recombination, which enhances both voltage and current outputs (Niu et al., 2013).

Embedding MOF particles into soft matrices like PDMS or Ecoflex enhances conformal contact under mechanical stress, contributing to further charge generation efficiency improvements (Dharmasena et al., 2017).

Studies have shown that MOF-derived porous carbons or metal-oxide composites can combine the best of both worlds—high porosity and conductivity. Such materials can notably elevate charge injection and retention (Dhal et al., 2024; Potu et al., 2023). Introducing heteroatoms (such as F, Cl) into MOFs like ZIFs improves electron affinity and charge polarization. ZIF-8-Cl variants reached record-high V_{OC} values, highlighting the effectiveness of chemical functionalization (Noman et al., 2024).

Layering MOF films directly onto flexible conductors (e.g., ITO, silver nanowires) via in-situ growth techniques or interfacial bonding enhances triboelectric output through increased charge transfer efficiency and reduced interfacial losses.

The integration of MOFs into complex device structures, e.g., hybrid TENG–supercapacitor or freestanding and rotational modes, enables multifunctionality, energy storage coupling, and adaptability to a broad range of mechanical excitations

Despite impressive strides, current limitations include:

- **Humidity Sensitivity:** MOF surfaces may adsorb water, altering their triboelectric and dielectric properties. Hydrophobic surface treatment or MOF encapsulation is needed to maintain performance.
- **Scalability and Cost:** The complexity and cost of MOF synthesis need to be addressed. Use of high-throughput or continuous flow methods (e.g., supercritical CO_2) offers potential.
- **Mechanical Durability:** Long-term triboelectric cycling under variable mechanical strain requires robust polymer–MOF composites and stress-relief architectures.

Future innovation in MOF-based triboelectric nanogenerators is poised to benefit from several cutting-edge strategies. First, AI-guided MOF discovery will leverage machine-learning algorithms and high-throughput computational screening to identify frameworks with optimal dielectric constants and polarizabilities, dramatically shortening the path from concept to experimental realization (Noman et al., 2024).

Second, hierarchical hybrids that integrate MOFs with conductive two-dimensional materials such as graphene or MXenes promise synergistic enhancements: the innate porosity and tunable chemistry of MOFs combined with the exceptional conductivity and mechanical resilience of 2D layers can push charge density and output power well beyond current benchmarks (Khandelwal et al., 2019; Dudem et al., 2018). Third, functionally graded MOF layers, fabricated to exhibit systematic gradients in pore size, chemical functionality, or polarity, offer a localized approach to charge generation and retention—akin to the band-gap engineering used in advanced semiconductor devices; by tailoring these gradients, one can finely control where and how triboelectric charges accumulate and dissipate under mechanical deformation (Yuan et al., 2022). Finally, by integrating MOF-TENG elements directly with sensing modalities such as gas- or bio-sensors, researchers can create self-powered, multifunctional platforms whose responsive MOF chemistries not only harvest energy but also transduce environmental or biochemical signals, opening avenues for wearable diagnostics, environmental monitoring, and Internet-of-Things applications.

5.2 Integration with Other Systems

Triboelectric nanogenerators (TENGs) offer unique capabilities in converting mechanical energy into electricity through contact-induced electrification and electrostatic induction. However, their typically high-voltage but low-current output can limit standalone applicability. To overcome such constraints, integrating TENGs with other energy harvesting mechanisms, such as piezoelectric, electromagnetic, thermoelectric, and photovoltaic systems, has emerged as a promising route for enhancing performance, broadening operating environments, and achieving energy redundancy and self-sustainability.

The most common integration involves coupling TENGs with piezoelectric nanogenerators (PENGs). Both devices respond to mechanical stimuli, but with different mechanisms: TENGs utilize contact electrification and charge transfer, while PENGs exploit internal dipole alignment under mechanical strain. These hybrid configurations can simultaneously leverage the high voltage of TENGs and the higher current output of PENGs, achieving a synergistic enhancement in total power density

and bandwidth of response. For instance, Yao, Ji, and Pu (2019) demonstrated a self-powered broadband vibration sensor based on a hybrid triboelectric–piezoelectric nanogenerator that delivered more than $2\times$ enhancement in electrical output compared to individual systems and maintained performance across a wide frequency range (Yao et al., 2019). Likewise, Jeong, Han, and Lee (2020) incorporated lead-free piezoelectric ceramics into a hybrid nanogenerator, significantly increasing power density and broadening frequency sensitivity, highlighting the potential of such systems for wearable and biomedical applications (Jeong et al., 2020).

Hybrid systems can be arranged in parallel or series electrical configurations, depending on desired output characteristics. Structurally, layered configurations are often used, with TENG components placed on flexible substrates above or below the PENG layer. Alternatively, concentric or coaxial geometries are adopted in cylindrical or tubular hybrid devices for rotational or vibrational environments. Mechanical decoupling and mechanical rectification mechanisms are also incorporated to minimize internal interference between TENG and PENG modules. Recent studies also emphasize microstructural alignment to optimize hybrid performance. Mode-dependent surface patterning, micro-asperity matching, and materials with complementary triboelectric and piezoelectric properties (e.g., BaTiO₃/PDMS, ZnO/PU composites) enhance interface contact quality and maximize energy transduction across both mechanisms (Kang et al., 2022).

Hybrid TENG–PENG systems have found significant applications in human motion detection, biomechanical sensors, ocean wave energy harvesting, and flexible electronics. In many cases, TENGs provide initial voltage spikes for signal generation, while PENGs contribute to sustaining current over time. Such systems ensure reliable output even in varied or low-motion environments, thereby expanding the operational resilience of self-powered systems.

Furthermore, the inclusion of both harvesting mechanisms creates fault tolerance—if one mechanism underperforms due to environmental variability, the other may compensate. This is especially valuable in outdoor, wearable, or remote-monitoring applications, where stability and continuity of energy supply are critical. As the demand for autonomous and sustainable electronic systems grows, hybrid energy

harvesting architectures that combine multiple transduction mechanisms such as triboelectric, piezoelectric, electromagnetic, thermoelectric, and photovoltaic, have garnered significant research attention. These hybrid systems aim to overcome the limitations of individual energy harvesters by broadening energy source compatibility, improving output stability, and enhancing total energy conversion efficiency.

Hybrid energy harvesters integrate triboelectric, piezoelectric, and electromagnetic mechanisms to capture mechanical energy across a broad range of frequencies and motion types. Triboelectric nanogenerators (TENGs) excel at converting low-frequency stimuli into high-voltage outputs but typically suffer from low currents, whereas electromagnetic generators (EMGs) deliver higher currents at elevated frequencies, and piezoelectric nanogenerators (PENGs) provide stable current outputs under strain. By combining these devices, a single motion event can simultaneously activate all three generators, producing a total electrical output that exceeds the sum of each component's contribution, a phenomenon known as the synergistic output effect (Yao et al., 2019; Jeong et al., 2020). Such hybrid systems ensure continuous functionality across diverse operational scenarios—from wearable electronics that harness bending (TENG), stretching (PENG), and vibration (EMG) to power biosensors or wireless modules (Pu et al., 2017), to marine buoys that exploit both vertical and lateral wave motions to drive parallel TENG and EMG units for remote monitoring (Cao et al., 2021). In smart infrastructure applications, embedding TENG–PENG–thermoelectric assemblies within buildings and bridges enables maintenance-free sensing by capturing ambient vibrations and temperature gradients (Jeong et al., 2020). Finally, coupling TENGs with photovoltaic cells leverages both mechanical and solar inputs for round-the-clock energy harvesting, as demonstrated by hybrid wind-vibration and solar panels that sustain power generation under fluctuating environmental conditions (Liu et al., 2022). Continuous development of multimodal harvesters promises robust, versatile power solutions for next-generation self-powered systems.

5.3 Scaling Up

Recent advancements have demonstrated the viability of scaling ZIF production economically and sustainably. Mechanochemical synthesis techniques have enabled kilogram-scale ZIF-8 production under solvent-free conditions, yielding high crystallinity and low cost per kilogram (Dhal et al., 2024). Concurrently, continuous-flow processes have achieved production rates exceeding $20 \text{ kg}\cdot\text{m}^{-3}\cdot\text{day}^{-1}$ while maintaining BET surface areas above $1500 \text{ m}^2/\text{g}$, essential for charge-storage enhancement in triboelectric applications (Noman et al., 2024). Composite fabrication for flexible TENG architectures now employs scalable methods such as spray deposition, doctor-blading, and roll-to-roll UV embossing; for example, fingerprint-mimicking ZIF-67/decorated films have been produced over square-meter areas with consistent electrical performance and mechanical durability (Chandrasekhar et al., 2024). Finally, long-term device integration studies reveal that ZIF-polymer composites sustain high voltage outputs ($\sim 300 \text{ V}$) and power densities ($\sim 600 \text{ mW}/\text{m}^2$) over tens of thousands of cycles, underscoring their endurance for field deployment in wave and structural-harvesting applications (Potu et al., 2023).

In the application potential in urban energy solutions, urban landscapes abound with mechanical energy sources walking footpaths, cycling lanes, vehicle traffic, HVAC infrastructure, and building oscillations. Embedded TENGs in sidewalks and cycling paths have demonstrated power densities of $5\text{--}30 \text{ mW}/\text{m}^2$ at pedestrian traffic speeds of $1\text{--}2 \text{ m/s}$ (Fan et al., 2012; Han et al., 2018). Panels installed on bridge expansion joints harvest vibrations to power structural monitoring sensors, providing continuous self-powered surveillance (Jeong et al., 2020; Yao et al., 2019). In addition, rooftop rain harvesting systems fitted with water-activated TENGs produce $0.1\text{--}0.3 \text{ mW}$ per 100 mL rain events sufficient for powering overflow sensors and urban indicators (Cao et al., 2021; Xu et al., 2017). These systems convert rainfall kinetic energy into usable electricity, integrating seamlessly into stormwater infrastructure.

Hybrid urban deployment offers that multipurpose platforms like rooftops and walls can co-locate TENGs, photovoltaic cells, and thermoelectric generators (TEGs), maximizing energy capture from sun, wind, temperature gradients, and mechanical

vibrations (Khandelwal et al., 2019; Noman et al., 2024). Moreover, lightweight ZIF-coated textile TENGs embedded into public transit seating have harvested up to 15 μW per passenger ride, which could scale to power lighting or charging ports in buses or trams (Barsiwal et al., 2022). Integrated into self-powered bike helmets, the harvested energy supports safety sensors and wireless indicators (Potu et al., 2023). The Table 5.3 displays the challenges, strategies, and future outlook for obtaining the TENG energy system from the ZIF-MOFs.

Table 5.3: Challenges, Strategies, and Future Outlook

Challenge	Strategy	Outcome
Moisture & UV stability	Hydrophobic coatings and UV-stabilizers	>85% output retention over 6 months (Zhang et al., 2024)
Scalable patterning	Laser-etching on roll-to-roll systems	5x increased output at 100 cm/s pedestrian flow (Nguyen et al., 2023)
Economic integration	Hybridizing ZIF production with EMG/Wind, leveraging cost-pooling	\$30/m ² module cost plus power from micro-wind turbines
Smart power management	AI-controlled impedance matching and storage selection	Stable microgrid output under variable stimuli

Chapter 6

Conclusion

In this study, we systematically investigated the integration of zeolitic imidazolate framework (ZIF) metal–organic frameworks—specifically ZIF-8 and ZIF-67—into triboelectric nanogenerators (TENGs) and demonstrated their superior performance compared both to conventional polymer–metal TENGs and across two distinct application scenarios. First, a hybrid-mode ZIF-8 TENG was developed for marine energy harvesting, combining vertical contact–separation and lateral sliding mechanisms within an accordion-folded 2×5 cm thin-film architecture on copper tape. Under a 2 Hz wave-simulating actuation, this device consistently produced an open-circuit voltage of 195 V and an output power of 35 μ W. Second, we designed a shoe-sole–integrated ZIF-67 TENG that exploits purely contact-mode operation on an aluminum substrate. During human gait, this wearable generator delivered peak voltages of 36 V and up to 28 μ W of power, sufficient to drive Bluetooth beacons, inertial sensors, or haptic feedback modules without external batteries.

The electrical outputs achieved in our ZIF-based devices represent a marked improvement over many reported TENGs that employ standard triboelectric pairs such as polystyrene–aluminum or PTFE–aluminum. Typical vertical contact–separation TENGs in the literature generate peak voltages in the 100–150 V range and power levels of 10–20 μ W under similar testing conditions. By contrast, the inclusion of ZIF-8 and ZIF-67 thin films owing to their high intrinsic surface area, tunable pore structures, and favorable electron-affinity mismatches yielded 20–50 % higher voltages and power outputs. Moreover, ZIF-8’s outstanding hydrolytic stability rendered the marine TENG resistant to saline corrosion over extended cycling, while ZIF-67’s optimized grain boundaries and elevated electron affinity enhanced charge separation during compressive loading in the shoe-sole application. These material-driven gains highlight the unique advantages of MOF coatings versus purely polymeric triboelectrics and underscore the value of porous crystalline frameworks in TENG design.

Our combined experimental and computational investigations elucidated the mechanisms by which ZIF microstructure governs triboelectric behavior. Single-crystal X-ray diffraction (XRD) revealed highly oriented pore channels in ZIF-8 films that align preferentially when deposited on flexible copper tape, creating anisotropic pathways for charge transfer. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirmed that ZIF-8 and ZIF-67 coatings exhibit nanoscale surface roughness (peak-to-valley heights up to ~550 nm) and well-defined grain boundaries, respectively. Density Functional Theory (DFT) calculations further demonstrated that these structural features generate localized surface-potential enhancements: aligned ZIF-8 pore axes concentrate electric fields under mechanical deformation, while ZIF-67 grain interfaces serve as charge-trapping sites that prolong charge retention during separation. Together, these insights provide a mechanistic rationale for the observed boosts in output voltage and power, and they establish clear design rules for future MOF-TENG optimization.

The power density levels demonstrated 95 mW/m² of ZIF-67 for marine energy harvesting and 28 mW/m² for biomechanical harvesting that are directly applicable to a range of low-power electronic systems. For instance, the ZIF-8 marine TENG producing 195 mW/m² could continuously sustain coastal monitoring buoys, subsea sensor arrays, or navigation aids by charging a small supercapacitor bank, while the ZIF-67 insole generator can maintain wearable health-monitoring devices or BLE beacons during daily activities. The modular nature of the accordion-folded design permits straightforward series or parallel interconnection to meet varying voltage and current requirements, enabling seamless scaling for larger installations or higher-current applications. Moreover, both devices rely on low-cost, solution-processable MOF syntheses and simple lamination steps, suggesting clear pathways to roll-to-roll manufacturing or inkjet-printing of TENG films at industrial scale.

Therefore, this study is the first to integrate an accordion-patterned ZIF-67 thin film on an aluminum substrate into a shoe sole, demonstrating the originality of our thin-film approach. Our spin-coated ZIF-8 hybrid TENG achieved a peak power density of 803 mW/m² surpassing typical literature benchmarks and its implementation of spin-coated MOF films on metal electrodes represents an innovative design. Moreover, the

accordion-inspired ZIF-67 TENG architecture underscores a novel wearable energy-harvesting configuration that, to our knowledge, has not been previously reported.

Building on these findings, several avenues for further enhancement emerge. Surface functionalization of ZIF-8 and ZIF-67 for example, grafting electron-donating or -withdrawing groups could further tailor triboelectric polarity and boost charge density. Compositing ZIF films with conductive nanofillers (e.g., graphene or MXene) may improve charge transport and mechanical robustness. Process-scale innovations such as roll-to-roll deposition or automated pleating equipment would facilitate large-area fabrication and reduce unit costs. Integration with advanced power-management circuits incorporating maximum-power-point tracking (MPPT), low-dropout regulators, and thin-film supercapacitor arrays will enable more efficient and stable DC outputs suitable for intermittent or high-burst loads.

Beyond hardware improvements, long-term environmental testing is essential to validate device resilience under real-world conditions such as biofouling in the marine environment or mechanical abrasion in footwear. Life-cycle assessments and techno-economic analyses will clarify the sustainability and cost-benefit profiles of ZIF-TENG systems compared to conventional battery or solar solutions. Finally, the overarching design principles established here for pore alignment, surface morphology control, and MOF-polymer hybridization can be extended to other MOF families or two-dimensional frameworks, opening a broad frontier for next-generation, self-powered devices.

This thesis delivers a comprehensive framework, from microstructural characterization through theoretical modeling to real-world proof-of-concept, demonstrating that ZIF-based TENGs can meaningfully outperform traditional triboelectric systems in both marine and wearable contexts. By validating the crucial role of pore architecture and grain structure in charge generation and by showcasing scalable device architectures, this work lays the groundwork for both academic exploration and industrial adoption of MOF-enhanced energy harvesters. As society increasingly seeks sustainable, maintenance-free power solutions for distributed electronics, the strategies and insights presented here position ZIF-MOF TENGs as a promising and versatile platform for the energy-harvesting technologies of tomorrow.

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<https://doi.org/10.1021/nl4001053>

Appendices

Appendix A Placement of Large Scale Visual Materials:

1. Full-text paper

Kurt Erdal, Çoban Mustafa Burak, Aykaç Ahmet, Yakali Gül , Ho-Mof-Metal–Organic-Framework-Based Triboelectricnanogenerator For Self-Powered Devices, 10.12.2024, 3th International Scientific Research Conference, Türkiye.

2. 1001 - BİLİMSEL VE TEKNOLOJİK ARAŞTIRMA PROJELERİNİ DESTEKLEME PROGRAMI (2025-1)

Zeolit İmidazolat Çerçeve Yapısı (ZIF) ve Geri Dönüştürülebilir Malzeme Tabanlı Triboelektrik Nanogeneratörlerle Sürdürülebilir Temiz Enerji Üretimi

ARDEB PBS
Proje Başvuru Sistemi

Ana Sayfa GÜL ÖZKAN Çilek

Başvurularım (0) Yeni Destek Başvurusu E-İmza Süreci ARDEB Proje Görevlerim Kuruluş Yetkilisi

Aktif Başvurularım

Proje başvuru kaydı bulunmamaktadır.

Önceki Başvurularım

Proje Id: 864579
Program Adı: 1001 - BİLİMSEL VE TEKNOLOJİK ARAŞTIRMA PROJELERİNİ DESTEKLEME PROGRAMI
Çağrı Adı: 1001 (2025-1)
Proje Başlığı: Zeolit İmidazolat Çerçeve Yapısı (ZIF) ve Geri Dönüştürülebilir Malzeme Tabanlı Triboelektrik Nanogeneratörlerle Sürdürülebilir Temiz Enerji Üretimi
Proje Yöneticisi/Yürütücüsünün Adı Soyadı ve Ünvanı: GÜL ÖZKAN
Başvuru Tarihi: 27.03.2025 15:16:12
Başvuru Tamamlanma Tarihi: 27.03.2025 18:47:26
Proje Dosyaları: Dosyaları Göster
Proje Durumu: Bilimsel Değerlendirme Sürecinde
Proje Başvurusu Elektronik İmza Durumu: Elektronik İmza Süreci Tamamlandı

Türkiye Bilimsel ve Teknolojik Araştırma Kurumu. Her hakkı saklıdır. © 2013 - 2025

3.

Proje No	Proje Adı	Proje Karar Durumu	Detay Durumu	Proje Türü	Proje Başlama Tarihi	Proje Bitiş Tarihi	Proje Süresi	Proje Görevi	Toplam Bütçe	Kalan Bütçe	İşlemler
1	UIO-66 ve MIL101(Fe) Tabanlı Metal-Organik İskeletlerin Sentezi, Karakterizasyonu ve Triboelektrik Nanogeneratörlerde Sürdürülebilir Enerji Üretimi için Performans Analizi	Değerlendiriliyor	Bap Ofis Ön Kontrol	ALT			12 Ay	Yurutucu	93,085.26 TL	93,085.26 TL	  

1 adet kayıttan 1 - 1 arası

Appendix B Publications from the Thesis

1. Submitted Manuscript

Incomplete submissions (0) Under processing (1) Website Online (0) Rejected / Withdrawn / Archived (0)					
Manuscript ID	Journal	Section / Special Issue	Title	Status	Submission Date
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