MOF-Based Bioelectronic Supercapacitors

*Begüm Sarac, Seydanur Yücer, and Fatih Ciftci**

Metal-organic frameworks (MOFs) represent a highly promising material class for bioelectronic supercapacitors, characterized by their adjustable structures, extensive surface areas, and superior electrochemical properties. This research explores the synthesis and incorporation of MOF-based materials into bioelectronic devices aimed at energy storage and biosensing applications. The focus is on improving the electrochemical performance of MOFs while preserving their structural integrity through functionalization with biocompatible polymers and conductive materials. The resulting MOF-based bioelectronic supercapacitors exhibit significant improvements in specific capacitance, energy density, and cycling stability. Additionally, the inclusion of bioreceptors allows for the simultaneous detection of biochemical signals alongside energy storage, thus enabling innovative applications in wearable electronics and health monitoring systems. These results suggest that MOF-based supercapacitors have the capacity to fulfill energy storage needs while also advancing bioelectronics by merging energy and sensing capabilities.

1. Introduction

Metal-organic frameworks (MOFs) have attracted significant attention in energy storage research due to their distinctive characteristics, including high surface area, adjustable porosity, and strong electrochemical properties.[1] These features make MOFs especially well-suited for use in energy storage devices, particularly in bioelectronic applications where both energy storage and biosensing capabilities are essential.[2] The incorporation of MOFs into bioelectronic supercapacitors enables the creation of multifunctional devices that can effectively store energy while simultaneously detecting biochemical signals.[3] Recent studies have demonstrated that enhancing MOFs with biocompatible polymers and conductive materials greatly boosts their stability and electrochemical performance, addressing challenges faced by traditional supercapacitors in bioelectronic applications.[4] These modifications not only improve the specific capacitance, energy density, and cycle life of MOF-based supercapacitors but also enhance their resistance to environmental factors, resulting in more stable and dependable energy storage solutions. This advancement makes them particularly suitable for applications such as wearable devices and health monitoring systems.[5] Incorporating MOFs into bioelectronic supercapacitors offers the possibility of developing a multifunctional platform that integrates both energy storage and biochemical sensing capabilities within a single device. This study aims to contribute to the advancement of energy storage and biosensing technologies by focusing on the synthesis, functionalization, and application of MOF-based materials in bioelectronic supercapacitors. The findings are expected to drive the creation of next-generation bioelectronic devices that could significantly influence fields such as healthcare, wearable technologies, and beyond.

2. Structural and Functional Properties of MOF-Based Bioelectronic Supercapacitors

2.1. Chemical and Physical Characteristics of MOFs

MOFs are highly regarded for their ability to achieve optimal performance through careful selection of linkers and metal nodes. A range of synthetic methods has been employed to alter the chemical composition, stability, particle size, and flexibility of these frameworks. Additionally, MOFs can undergo post-synthetic modifications that further enhance their properties, which may involve adjusting or removing specific binder or node components. The surface chemistry of MOFs can also be fine-tuned by managing their crystallographic phases and controlling the size and morphology of the crystallites. This ability to modify various properties allows for effective management of guest-host interactions, especially in energy storage applications, highlighting a key advantage of this unique class of porous materials.

The electrochemical stability of MOFs can be improved through the careful selection of synthetic parameters. To ensure thermal and chemical stability, it is beneficial to choose structures

---

B. Sarac, S. Yücer, F. Ciftci
Faculty of Engineering
Department of Biomedical Engineering
Fatih Sultan Mehmet Vakıf University
Istanbul 34015, Turkey
E-mail: faciftcii@gmail.com

F. Ciftci
Department of Technology Transfer Office
Fatih Sultan Mehmet Vakıf University
Istanbul 34015, Turkey

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202412846

DOI: 10.1002/smll.202412846

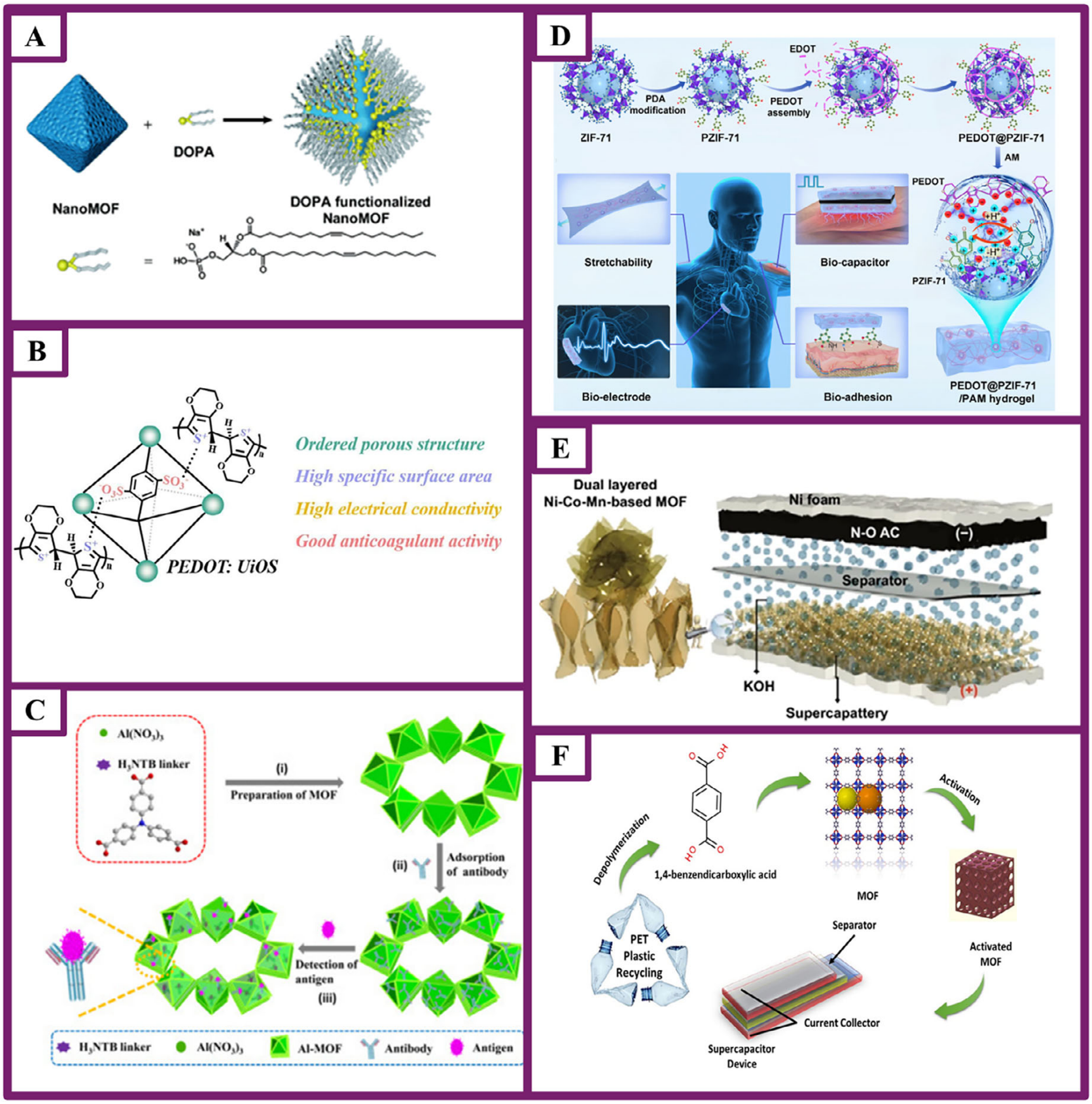

Figure 1. A) Schematic summary, Zr-based MOF nanoparticles that have been extensively modified on their surface with 1,2-dioleoyl-sn-glycero-3-phosphate (DOPA) demonstrated significantly altered colloidal characteristics. This study concludes that post-synthesis modifications can effectively tailor the surface chemistry of nano MOFs by coordinating with exposed metal-containing sites, all while preserving their crystallinity and sustained porosity.[8] Copyright 2015 Wiley. B) Schematic abstract, Zr-based MOFs were shown to increase the surface area, conductivity, and anticoagulant activity of PEDOT.[9] Copyright 2024 Elsevier. C) Schematic summary illustrates the successful application of two immunosensors constructed from aluminum-based metal-organic frameworks featuring 4,4‘,4’’-nitrilotribenzoic acid (H3NTB) for evaluating food safety.[10] Copyright 2017 Elsevier. D) Schematic summary describes the creation of a core-shell redox-active system featuring a polydopamine-modified zeolitic imidazolate framework (MOF) ZIF-71 as the core and a PEDOT shell, designed for stretchable and conductive hydrogels.[11] Copyright 2023 Royal Society Of Chemistry. E) In this study, a novel class of binder-free, dual-layered Ni–Co–Mn-based MOFs (NCM-based MOFs) with 3D-on-2D nanoarchitectures was investigated, synthesized via a polarity-induced solution-phase method to achieve high-performance supercapatteries.[46] Copyright 2021 SPRINGER NATURE. F) The schematic summary focuses on the synthesis of Zr-MOF from PET bottles and highlights its high surface area and excellent electrochemical properties for next-generation supercapacitors.[12] Copyright 2024 Elsevier.

that include redox-inactive nodes and shorter, more rigid linkers. At the same time, the high porosity and flexibility of these materials enable efficient ion storage and transport. The mechanical properties of MOFs can be adjusted by incorporating flexible linkers, tuning host-guest interaction strengths, designing multi-metal frameworks, and manipulating crystal sizes. It's essential to consider the structural stiffness of electrodes, particularly concerning dendrite formation. The inherent flexibility of MOFs can help maintain structural integrity in devices subjected to volume fluctuations. Additionally, stimulus-responsive flexible MOFs are crucial for safety applications, as they can activate a "switch-off" mechanism in response to various stimuli, including temperature, voltage, or mechanical forces.[6]

2.1.1. High Surface Area and Porosity

MOFs have gained significant attention as promising materials for electrochemical energy storage (EES), particularly in supercapacitor electrodes. Their exceptionally high surface area and well-organized micro/mesoporous structures contribute to enhanced capacitance by increasing the number of active sites and improving ion transport, ultimately leading to high power density. Optimizing the pore architecture of MOF-based supercapacitors is crucial, and various approaches—such as reticular chemistry, multiscale pore design, advanced synthesis techniques, and post-synthesis modifications—are utilized to refine their structure and performance.

To further boost the efficiency of supercapacitors, MOFs can be engineered with conductive frameworks, incorporated guest molecules, or redox-active centers. Additionally, converting MOFs into highly porous carbon derivatives or integrating them into hybrid structures has proven to improve capacitance and extend their cycle stability. A comprehensive evaluation of pore design strategies is essential to maximize the potential of MOFs in supercapacitor applications and improve their overall electrochemical performance.[7]

2.1.2. Functional Groups and Surface Modifications

MOFs are an important focus of research in nanotechnology and materials science. In recent studies, scientists have developed a novel approach for modifying the outer surfaces of nanoscale MOFs using 1,2-dioleoyl-sn-glycero-3-phosphate (DOPA). This investigation involved the synthesis of a series of zirconium-based nano MOFs that share the same topology, which were subsequently conjugated with DOPA. This process led to the formation of stable, well-dispersed colloidal solutions.

Analytical results showed that the porosity of these structures remained unchanged after surface functionalization, indicating that DOPA primarily affects the outer surfaces. Additionally, the research revealed a relationship between the density of DOPA on the surfaces of the nanoscale MOFs and the concentration of metal nodes in each framework. As a result, this method opens up new avenues for the synthesis and study of various nanoscale MOFs as stable colloidal materials, highlighting their potential for enhanced functionality.[8] (**Figure** 1A).

2.2. MOFs as Electrode Materials Suitable for Bioelectronic Applications

2.2.1. Zirconium-Based MOF

Zirconium-based metal-organic frameworks (Zr-MOFs) have gained attention for their remarkable stability and structural diversity, making them suitable for various electrochemical and biosensing applications. Wang et al. to address the problem of reduced electrical conductivity in PEDOT due to the incorporation of non-conductive additives, Wang et al. developed a new electrode material called PEDOT:UiOS. This material contains zirconium-based sulfonic acid MOFs (UiOS) as additives that contribute to the formation of a well-organized porous structure within PEDOT. The resulting structure enhances electrolyte penetration and ion migration during energy storage processes, resulting in improved electrochemical performance. PEDOT:UiOS has been successfully applied in flexible semi-solid-state supercapacitors and has shown remarkable improvements in anticoagulant properties, electrochemical efficiency, and cycling stability. In particular, the coagulation time was increased to 44.9 s, a power density of 400.0 μW cm^{-2} was achieved at an energy density of 3.56 μWh cm^{-2}, and the material retained 86.17% of its initial capacity after 2000 cycles. This advanced electrode material has great potential to alleviate energy limitations and improve blood safety in implantable energy storage devices (Figure 1B).[9]

2.2.2. Copper-Based MOF

Copper-based MOFs have demonstrated significant potential in biomedical applications, particularly in drug delivery, cancer therapy, and biosensing. In this similar study, it examines the recent developments and applications of copper-based MOFs in biological contexts. It highlights the advantages of these frameworks in various fields such as drug delivery, cancer therapy, sensing, and antimicrobial applications.[13] Additionally, the paper discusses the significant role of advanced composite materials, such as MOF polymers, in tailoring materials for specific uses. A notable innovation is a flexible biosensor capable of real-time monitoring of ascorbic acid (AA) levels in sweat. This biosensor, designed to be mounted on the skin and integrated with MOF-derived composites, features an imperceptible form factor that conforms to the natural contours of the skin. The addition of a copper-based MOF stabilized with poly(3,4-ethylenedioxythiophene) enhances the biosensor's sensitivity and lowers the detection limit for AA. The lightweight, wearable device incorporates a miniaturized flexible circuit for wireless communication. Structural and electrochemical evaluations validate the biosensor's critical attributes, including sensitivity, reversibility, and stability. Human subject trials indicate that the biosensor effectively tracks fluctuations in sweat AA levels during food consumption and physical activity. In summary, this technology represents a promising approach for scalable health monitoring, featuring adaptive and user-friendly capabilities that hold significant potential for evaluating metabolic processes and managing health conditions.[14]

2.2.3. Iron-Based MOF

Iron-based MOFs (Fe-MOFs) offer significant advantages for biomedical research due to their high stability, low toxicity, and strong electrochemical properties. Park et al. described a class of mixed-valence MOFs that exhibit improved conductivity via chemical oxidation. These materials, termed $Fe(tri)_2(BF_4)_x$, were synthesized by oxidizing the initially poorly conducting iron(II) framework $Fe(tri)_2$. The most oxidized version, $Fe(tri)_2(BF_4)_{0.33}$, showed a significant increase in conductivity, reaching

0.3(1) S cm^{-1} at room temperature, an eightfold improvement over the original material. Characterization techniques revealed that the improved conductivity is due to the intermittent charge transfer occurring between the mixed valence FeII/III centers. Mössbauer spectroscopy also confirmed the presence of valence-delocalized FeII/III species, a remarkable discovery for a metal-organic framework. These results provide valuable insights into the charge transport mechanisms in MOFs and potentially expand their use in electronic and electrochemical applications.[15]

2.2.4. Aluminum-Based MOF

Aluminum-based MOFs are not inherently pseudocapacitive, their electrochemical activity can be enhanced through hybridization with carbon-based materials or conductive polymers. Although aluminium-based and copper-based MOFs do not inherently exhibit strong pseudocapacitive behavior, they can function as electrochemically active materials in supercapacitors when appropriately modified. Their conductivity can be enhanced through the incorporation of carbon-based materials, conductive polymers, or thermal treatments, leading to improved performance. Copper-based MOFs, in particular, may display pseudocapacitive characteristics under specific conditions due to Cu^{2+}/Cu^{+} redox activity, whereas aluminium-based MOFs primarily contribute to double-layer capacitance by offering a high surface area and porous structure. While these MOFs are not intrinsically pseudocapacitive, they can be optimized for supercapacitor applications by integrating them into hybrid or composite electrode systems. In this similar study the successful synthesis of aluminum-based MOFs, specifically the 515- and 516-MOFs combined with 4,4′- and 4″-nitrilotribenzoic acid (H_3NTB), provides an effective strategy for evaluating food safety. These synthesized MOFs exhibit crucial characteristics such as enhanced thermal and physicochemical stability, notable electrochemical activity, and favorable biocompatibility. Among them, the 516-MOF has shown promising selective biosensing capabilities for analytes detected using electrochemical methods. The electrochemical biosensor utilizing 516-MOF has achieved remarkable selectivity, even in the presence of various interfering substances, alongside high sensitivity with detection limits of 0.70 pg mL^{-1} for vomitoxin and 0.40 pg mL^{-1} for salbutamol. In summary, this innovative approach presents considerable potential for the efficient and user-friendly detection of toxic and harmful residues in food products, highlighting its high sensitivity and excellent selectivity[10] (Figure 1C).

2.2.5. Hybrid MOF

Hybrid MOFs combine the unique advantages of MOF structures with additional functional materials, enhancing their performance in biosensing applications. A hierarchical FeCo-MIL-88 (FC-MOF)-derived $CoFe_2O_4$ and $NiMn_2O_4$ (CFO@NMO) composite was successfully synthesized using a hydrothermal approach. The synthesis process and formation mechanism of the composite were systematically investigated. Structural and morphological analyses were conducted using XRD, XPS, FESEM-EDS, HRTEM, and nitrogen adsorption-desorption isotherms. The incorporation of $CoFe_2O_4$ (CFO) and $NiMn_2O_4$ (NMO) in the composite effectively enhanced its electrical conductivity, thereby improving its electrochemical performance. As a result, the CFO@NMO hybrid electrode exhibited a high specific capacity of 353.6 mAh g^{-1} and retained 86.1% of its capacity after 5000 galvanostatic charge–discharge (GCD) cycles. To capitalize on its exceptional cycling stability and high specific capacity, an aqueous electrolyte-based hybrid supercapacitor (HSC) was assembled using AC//NF as the negative electrode and CFO@NMO//NF as the positive electrode. The fabricated HSC delivered a specific capacitance of 312.8 F g^{-1}, retained 88.4% of its capacitance after 10000 GCD cycles, and exhibited an impressive energy density of 90.3 Wh kg^{-1} along with a power density of 12.9 kW kg^{-1}. The facile and cost-effective synthesis of the CFO@NMO composite, combined with its outstanding supercapacitor performance, highlights its significant potential for future energy storage applications.[16]

2.3. Electrical Properties of MOFs and Methods to Enhance Conductivity

2.3.1. Electrical Properties of MOFs

MOFs have garnered significant attention due to their tunable porosity, structural diversity, and potential applications in various electronic and energy storage devices. However, the inherently low electrical conductivity of conventional MOFs has limited their direct application in electronic and electrochemical systems. To address this issue, researchers have explored various strategies to enhance the electrical properties of MOFs, including mixed-valence systems, donor-acceptor frameworks, and ligand-based charge transport mechanisms. One of the most effective approaches to improving MOF conductivity is the mixed-valence strategy, where metal centers exhibit multiple oxidation states, facilitating charge transfer. A notable example is $Cu[Cu(pdt)_2]$ (pdt = 2,3-pyrazinedithiolate), synthesized by Takaishi et al., which demonstrated a conductivity of 6×10^{-4} $S\cdot cm^{-1}$ at 300 K, significantly surpassing traditional insulating MOFs. This system consists of 2D sheets connected through CuI and S atoms, forming a 3D network that supports charge hopping as the primary conduction mechanism. Beyond metal-centered charge transfer, the ligand-based mixed-valence strategy has also been explored. For instance, $(NBu_4)_2Fe_2(dhbq)_3$ ($dhbq^{2-}/^{3-}$ = 2,5-dioxidobenzoquinone/1,2-dioxido-4,5-semiquinone) exhibits an exceptionally high conductivity of 0.16 $S\cdot cm^{-1}$ at 298 K. In this system, charge transfer occurs between organic ligands rather than metal centers, demonstrating an alternative pathway for electrical conductivity in MOFs. Moreover, the redox tunability of these materials allows for fine control over their electronic properties, making them promising candidates for energy storage and sensor applications. Another approach to enhancing MOF conductivity involves the donor-acceptor (D-A) strategy, in which electron-rich (donor) and electron-deficient (acceptor) moieties are integrated into the framework to promote charge delocalization. A representative example is $Zn(DMF)_2(TTFTC)(DPNI)$, where tetrathiafulvalene-tetracarboxylate (TTFTC) serves as the donor and naphthalene diimide (NDI) in DPNI acts as the acceptor. The mixed stacking of these components facilitates charge transport, although its conductivity remains moderate due to the absence of a fully conjugated electronic structure. In addition to these intrinsic modifications, external factors such as guest molecule infiltration, doping, and post-synthetic modifications have been employed to enhance MOF conductivity. The incorporation of redox-active species, conductive polymers, or metal nanoparticles into MOF structures has been shown to improve charge transport properties, further expanding their potential applications in supercapacitors, batteries, and electrocatalysis. Overall, the electrical properties of MOFs are highly dependent on their structural design and electronic configuration. While conventional MOFs exhibit poor conductivity, recent advancements in mixed-valence frameworks, donor-acceptor systems, and ligand-based charge transport mechanisms have significantly improved their electrical performance. These developments pave the way for the integration of MOFs in next-generation electronic and energy storage devices, particularly in applications requiring high surface area and tunable conductivity.[17]

2.3.2. Methods to Enhance Conductivity

Solid materials exhibit two primary charge transport mechanisms: band-like transport and redox hopping. In most MOFs, substantial overlap between the metal ions and ligand orbitals leads to the creation of continuous conduction bands through covalent metal-ligand bonding. This band structure allows materials to be classified as insulators (with a bandgap ≈3.6 eV or greater), semiconductors (with a bandgap below ≈3.6 eV), or metallic conductors. With increasing temperature, metallic conductors show a decrease in conductivity, while semiconductors exhibit an increase. The conductivity of typical semiconductors follows the Arrhenius equation, where the activation energy corresponds to half of the bandgap. Apart from the band model, there is also a hopping mechanism in which charges are transported via phonon assistance. In this mechanism, conductivity is influenced by the dimensionality of the lattice (e.g., in 3D systems, $\alpha = 1/4$, consistent with the Mott model). This model suggests that rising temperatures enhance conductivity due to increased electron delocalization. Although most MOFs are either insulators or semiconductors, a growing number demonstrate metallic conductivity, with the hopping mechanism occasionally used to further explain conductivity behavior.[18]

Metal-organic frameworks have gained significant attention in energy storage and sensor technologies due to their large surface area, tunable pore structures, and high electrochemical activity. In recent years, the use of MOF-based materials as supercapacitor electrodes and electrochemical sensors has been increasing, with remarkable research findings emerging in this field. Specifically, supercapacitors developed using NiNiacin-MOF have shown promising results with a high specific capacitance (4500 F g^{-1}) and energy density (64.7 Wh kg^{-1}). However, the electrode performance of such MOFs largely depends on synthesis methods, surface modifications, and conductivity enhancement strategies. In this context, the applicability of NiNiacin-MOF-based electrodes for both supercapacitors and glucose sensors highlights the multifunctional potential of MOFs. Nevertheless, factors such as scalability in synthesis processes and long-term stability remain critical for their commercial feasibility.[19]

On the other hand, the integration of MOF-5/rGO nanocomposites in supercapacitors and glucose sensors demonstrates how hybridizing MOFs with conductive carbon-based materials improves electrochemical performance. The combination of MOF-5 with rGO enhances the active surface area, increasing both the specific capacitance (334 F g^{-1}) and sensor sensitivity. This underscores the vital role of carbon-based additives in overcoming the conductivity limitations of MOFs. However, further research is required to address issues related to the hydrothermal stability and electrochemical cycling durability of MOF-5.[20]

Additionally, electrochemical synthesis methods play a crucial role in advancing MOF-based electrodes. The development of MOF-based sensors modified with various metal nanoparticles indicates that integrating MOFs with metal nanoparticles effectively enhances conductivity. For instance, functionalizing Zn-based MOFs with silver and gold nanoparticles expands the active electrode surface area, thereby improving sensor performance. However, optimizing such hybrid structures for supercapacitors and maintaining long-term electrochemical stability remain areas for further exploration.[21] Overall, recent advancements in MOF-based supercapacitors and biosensor applications highlight the versatile potential of these materials. However, key challenges such as conductivity, stability, and scalability must be addressed for their commercial viability. In the future, functionalizing MOFs with carbon-based materials and metal nanoparticles will enable the development of more efficient and durable systems for both energy storage and bioelectronic sensor applications (**Table 1**).

3. Application of MOFs in Bioelectronic Supercapacitors

3.1. Performance Parameters of MOF-Based Electrodes

The electrochemical performance of MOF-based electrodes is influenced by their composition, structural properties, and modifications for enhanced energy storage applications. This section examines various studies on the optimization of MOF-based electrodes for supercapacitors, emphasizing their capacitance, stability, and energy storage capabilities. This study presents a composite electrode material that integrates cobalt intercalated Co-MOF with polyaniline (PANI) for use in supercapacitors designed to deliver consistent energy output. The cobalt-based MOF is characterized by a significant surface area and high porosity, which facilitate multiple pathways for charge storage and reversible faradic reactions, thereby enhancing electrochemical performance. While the Co-MOF alone exhibited a specific capacity of 55 C g^{-1} at a scan rate of 3 mV s^{-1}, this capacity was deemed insufficient for high-energy applications. To improve performance, a composite of the cobalt-based MOF and 50% PANI was created, resulting in a structure referred to as MOF/PANI. This composite demonstrated enhanced capabilities, achieving a specific capacity of 162.5 C g^{-1} at a current density of 0.4 A g^{-1} during galvanostatic charge-discharge (GCD) analysis. When integrated into a supercapacitor device,

Table 1. Electrode materials suitable and electrical properties, enhance conductivity, chemical– physical characteristics for bioelectronic applications of MOFS.

Heading		Description	Key Parameters	Example Values/Data	Refs.
Chemical and Physical Characteristics of MOFs		Characteristics of MOFs related to surface area, porosity, and surface modifications	Surface area ($m^2\ g^{-1}$), pore volume ($cm^3\ g^{-1}$), functional groups	Surface area: 1200–2000 $m^2\ g^{-1}$ Pore volume: 0.8–1.2 $cm^3\ g^{-1}$	[22]
	High Surface Area and Porosity	Importance of the high surface area and porous structure of MOFs in energy storage	Surface area, pore distribution, pore volume	Surface area: 1500 $m^2\ g^{-1}$ Pore volume: 1.0 $cm^3\ g^{-1}$	[23]
	Functional Groups and Surface Modifications	Effects of added functional groups and surface modifications on the electrical properties of MOFs	Type of functional group (carboxyl, amino, etc.), surface modification method	Carboxyl group addition Plasma surface modification	[24]
MOFs as Electrode Materials Suitable for Bioelectronic Applications		Types of MOFs based on different metals used as electrode materials	Conductivity, stability, biocompatibility	Zirconium MOF: 1.1 S cm^{-1} Copper MOF: 95% biocompatibility	[25]
	Zirconium-Based MOF	Preferred for bioelectronic applications due to high chemical stability	Conductivity, stability	Conductivity: 1.1 S cm^{-1} Stability: 98%	[26]
	Copper-Based MOF	High electrical conductivity and enhanced biocompatibility	Conductivity, biocompatibility	Conductivity: 1.5 S cm^{-1} Biocompatibility: 95%	[27]
	Iron-Based MOF	Used in sensing systems due to high magnetic properties	Magnetic moment, conductivity	Magnetic moment: 5 μB Conductivity: 0.8 S cm^{-1}	[28]
	Aluminum-Based MOF	Preferred for its lightweight and biocompatible structure	Stability, biocompatibility	Stability: 90% Biocompatibility: 97%	[29]
	Hybrid MOF	MOFs formed by combining two or more metals	Conductivity, stability	Conductivity: 2.0 S cm^{-1} Stability: 95%	[30]
Electrical Properties of MOFs and Methods to Enhance Conductivity		Techniques applied to enhance the electrical properties of MOFs	Electrical conductivity, doping agents	Conductivity: 1.2 S cm^{-1} Doping agent: Nitrogen	[18]
	Electrical Properties of MOFs	Electrical performance of MOFs in energy storage applications	Conductivity, dielectric constant	Conductivity: 1.0 S cm^{-1} Dielectric constant: 12	[31]
	Methods to Enhance Conductivity	Techniques used to improve MOF conductivity	Doping, addition of carbon-based materials	Doping agent: Nitrogen Graphene incorporation	[32]

the MOF/PANI electrode served as the positive electrode alongside activated carbon as the negative electrode, resulting in a specific capacity of 104.5 C g^{-1}, a specific energy of 23.2 W h kg^{-1}, and a power density of 1600 W kg^{-1}. Additionally, the composite reached an impressive energy density of 12.81 W h kg^{-1} with a peak power density of 4480 W kg^{-1}, highlighting the Co-MOF/PANI composite as a promising candidate for advanced energy storage systems.[33]

The performance of supercapacitors under extreme conditions, such as low temperatures, is a crucial factor in energy storage applications. Research has focused on developing MOF-based electrodes that retain high capacitance even at sub-zero temperatures. The development of supercapacitors with high performance at low temperatures represents a significant challenge in the field of energy storage. Z. Chen et al. present an effective strategy for the synthesis of hierarchical porous electrode materials (HTTP-M(Co/Ni)-CC) utilizing in situ grown 2D conductive dithiol cobalt/nickel and 2,3,6,7,10,11-triphenylenehexathiolate. The specific capacitance values of HTTP-Co-CC and HTTP-Ni-CC were determined to be 83.5 and 103.9 F g^{-1}, respectively, in the absence of binders or conductive additives at a temperature of −60 °C. In comparison with the room temperature capacitance values, the capacitance retention rates of these materials remain at 82.7% and 87.1%, respectively. This makes them unique MOF electrode materials for low-temperature energy storage. The exceptional performance at low temperatures can be attributed to three key factors: the increasing conductivity with decreasing temperature, the ease of mass transfer provided by the hierarchical pore structures, and the effect of the flexible porous carbon substrate, which offers buffer space for volume expansion. This research illustrates the potential of conductive dithiol MOF-based electrodes as a novel contender for high-performance energy storage at low temperatures and provides a promising avenue for the advancement of new active material families for supercapacitors.[34]

Enhancing the energy density of supercapacitors remains a primary goal in electrode material research. New MOF structures have demonstrated promising results in improving the specific capacitance and long-term stability of energy storage devices. The pursuit of high-performance electrode materials aimed at enhancing the energy density of supercapacitors is a crucial area of research. In this regard, the recently synthesized 3D MOF $[Mn(BGPD)(H_2O)_2]$ (Mn-BGPD; BGPD = N,N'-bis(glycinyl)pyromellitic diimide) stands out as a noteworthy candidate. When employed as an electrode material in supercapacitors, Mn-BGPD exhibits an impressive specific capacitance of 832.6 F g^{-1} at a current density of 1 A g^{-1} within a three-electrode configuration. Additionally, in asymmetric supercapacitor setups, it achieves a specific capacitance of 100 F g^{-1} and an energy density of 35.5 W h kg^{-1}. Its remarkable cycling stability, characterized by a capacitance retention of 46.7%, further highlights Mn-BGPD's potential as an effective electrode material for supercapacitors. Collectively, these results underscore the promise of MOF-based materials for advancing future energy storage technologies.[35]

Nickel-based MOFs are widely studied for their high surface area and porosity, which contribute to their potential as effective supercapacitor electrodes. However, their performance is often limited by poor conductivity, necessitating modifications to enhance their electrochemical properties. Ni-based MOFs are gaining attention as effective electrode materials for supercapacitors due to their large surface areas and high porosity. Despite these advantages, their poor conductivity often leads to unsatisfactory specific capacitance and rate performance. In this study, a straightforward hydrothermal method was utilized to create Co-doped 3D Ni-based MOFs (Co x-Ni-MOF, with x = 100n (Co/Ni) = 0.5, 2, and 5) in the form of flower-like hierarchical microspheres. The introduction of cobalt significantly enhances the electrochemical properties of the Ni-MOF, achieving remarkable specific capacitance values of 1300 F g^{-1} at 1 A g^{-1} and 1021 F g^{-1} at 10 A g^{-1}. Additionally, the Co-Ni-MOF exhibits impressive cycling stability, maintaining 71% of its original capacitance even after 3000 cycles. This enhanced performance can be attributed to the unique 3D flower-like structure, which increases the specific surface area and improves electrical conductivity, resulting in a remarkable energy density of 25.92 Wh kg^{-1} at a power density of 375 W kg^{-1}. These results underscore the potential of Ni-based MOFs for supercapacitor applications, highlighting their suitability for energy storage solutions.[36]

3.2. Integration of Biological and Electronic Functions

3.2.1. Combination of Biosensors with Supercapacitors

Biosensors are specialized devices designed to detect and measure specific biological molecules. They consist of two primary components: the bioelement, which interacts with the target analyte, and the transducer, which converts the biological signal into an electrical one. Based on the type of bioelement and transducer used, biosensors can be categorized into various types, including electrochemical, optical, piezoelectric, and thermal biosensors. Electrochemical biosensors convert chemical reactions into electrical signals, optical biosensors detect analytes through light interactions, piezoelectric biosensors translate mechanical changes into electrical signals, and thermal biosensors sense heat changes caused by biological reactions. These biosensors find applications in a wide range of fields, such as medical diagnostics, environmental monitoring, food safety, and biotechnology. For a biosensor to be effective, it must provide precise and consistent responses, remaining unaffected by external conditions. The field of biosensors is rapidly advancing, benefiting from innovations like miniaturization, the integration of the Internet of Things (IoT), artificial intelligence, and nanotechnology. These advancements are expanding the potential applications of biosensors, enabling the development of wearable health devices, enhanced environmental monitoring systems, and innovations in smart agriculture (**Table 2**).[37]

The increasing demand for dependable energy sources in wearable health monitoring devices has led to the innovation of self-powered sensing technologies. Recent advancements in this field have concentrated on leveraging multifunctional materials to improve overall system performance. Among these materials, MOFs have gained considerable attention in electrochemical sensors and energy storage systems, thanks to their high surface area, electrocatalytic properties, and compatibility with biological systems. Paul Nagarajan et al. explore a nanocomposite developed from MOF-5, a zinc-based metal-organic framework, combined with reduced graphene oxide (rGO). The performance of this nanocomposite was assessed for its use as a non-enzymatic glucose sensor and as a supercapacitor. By integrating MOF-5 with rGO, active sites are revealed, leading to a hybrid electrode that showcases outstanding glucose sensing performance. The MOF-5/rGO nanocomposite achieved a sensitivity of 5693.4 μA mM^{-1} cm^{-2} and demonstrated a low detection limit of 0.7 μM within a glucose concentration range of 0.005–5 mM. Additionally, it exhibited impressive super capacitive performance, with a specific capacitance of 334 F g^{-1} at a current density of 1 A g^{-1}. To further explore its potential as a self-powered glucose sensor, a prototype based on the MOF-5/rGO nanocomposite was developed. Overall, the MOF-5/rGO nanocomposite shows significant promise for both glucose detection and efficient energy storage.[20]

3.2.2. Potential Uses in Health and Medical Applications

Wearable electronic textiles, commonly referred to as e-textiles, have emerged as a promising solution for seamlessly integrating electronic health monitoring devices into our daily lives. However, the quest for high-performance and flexible energy storage solutions poses a significant challenge to the advancement of these technologies. H. Singh Jhinjer et al. introduce a straightforward methodology for designing and fabricating MOF-based smart wearable e-textiles intended for all-solid-state textile supercapacitors. The fabrication process focuses on creating highly flexible and washable e-textiles through techniques such as screen printing, pad-dry coating, and inkjet printing, using a standalone MOF. These e-textiles serve as electrodes for the all-solid-state textile supercapacitor. Notably, the fabricated supercapacitors achieved impressive areal capacitance values of $^{-1}$221.51, 359.4, and 353.5 mF cm^{-2} at a scan rate of 1 mV s^{-1} for screen printing, pad-dry coating, and inkjet printing, respectively. Energy densities were recorded at around 123.06 μWh cm^{-2} (screen print), 199.66 μWh cm^{-2} (coating), and 196.39 μWh cm^{-2} (inkjet print), while power densities reached as high as 55377 μW cm^{-2}. Remarkably, the supercapacitors demonstrated exceptional capacitance retention of ≈97.4–97.9% after 1000 cycles. The study also reported power densities of 5 μW cm^{-2} (screen print), 55291.54 μW cm^{-2} (coating), and 54385.38 μW cm^{-2} (inkjet print). These findings underscore the potential of MOF-based smart textiles in the realm of wearable electronics,

Table 2. The table summarizes the parameters of biosensors such as principle of operation, sensitivity, response time, cost, and usage areas.

Biosensor Type	Principle of Operation	Responsiveness	Response Time	Cost	Areas of Use	Refs.
Electrochemical Biosensor	Target molecule generates an electrochemical signal	Very high	Seconds to minutes	Low-medium	Glucose measurement, disease markers	[38]
Optical Biosensor	Light absorption, fluorescence or plasmonic change is measured	Very high	Milliseconds to seconds	Medium-high	DNA analysis, drug testing	[39]
Piezoelectric Biosensor	Mass variation affects the resonance frequency	Medium-high	Seconds to minutes	Medium	Air quality, toxin detection	[40]
Thermal Biosensor	Heat changes are detected	Medium	Minutes	Medium	Bacteria detection, biochemical analyses	[41]

particularly in developing high-performance energy storage solutions tailored for textile applications.[42]

Insulin, a hormone secreted by the pancreatic β cells, is essential for regulating blood glucose levels. It aids in transporting glucose into cells, where it can be stored as glycogen or converted into triglycerides. Insulin deficiency can lead to hyperglycemia and contribute to the onset of diabetes, making insulin detection a vital aspect of clinical diagnostics. In this similar study, they modified disposable gold electrodes for insulin detection using a composite of copper(II) benzene-1,3,5-tricarboxylate (Cu-BTC) and a leaf-like zeolitic imidazolate framework (ZIF-L). The aptamers were immobilized onto the Cu-BTC/ZIF-L composite through physical adsorption, allowing for specific interactions with insulin. The resulting apt sensor exhibited a wide detection range for insulin, spanning from 0.1 pM to 5 μM, with an impressive detection limit of 0.027 pM. Additionally, the apt sensor showed high specificity, reproducibility, and stability, along with promising applicability in human serum samples. For in vivo validation, Cu-BTC/ZIF-L composite-modified electrodes were implanted into both non-diabetic and diabetic mice, and insulin levels were measured using electrochemical techniques and enzyme-linked immunosorbent assays.[43]

3.3. Optimization of MOFs for Energy Storage and Bioelectronic Performance

Supercapacitors utilize two primary energy storage mechanisms: electric double-layer capacitance (EDLC) and pseudocapacitance. In the EDLC mechanism, energy is stored through the formation of a double layer of charge at the interface between the electrode and the electrolyte, with no chemical reactions involved. On the other hand, pseudocapacitance involves energy storage via faradaic redox reactions at the electrode surface. While EDLC does not require chemical processes, pseudocapacitance is characterized by these redox reactions. Many electrochemically active materials found in nature have shown potential for use as electrode materials in supercapacitors. Research has revealed that certain materials display EDLC behavior, while others exhibit pseudocapacitive properties. Carbon-based materials (such as carbon nanotubes, activated carbon, and carbon black) typically exhibit EDLC properties, while metal oxides and hydroxides are known for their pseudocapacitive characteristics. As a result, extensive research is being conducted to explore a variety of materials that could improve supercapacitor performance. One promising class of materials in this field is MOFs, which are being investigated as potential new electrode materials.[44]

Stretchable and conductive hydrogels are gaining recognition as innovative materials for wearable devices. However, traditional conductive hydrogels often face limitations due to their inadequate electroactivity and bio adhesiveness. This similar study introduces a mussel-inspired approach to create a specialized core–shell redox-active system. The system comprises a core made of zeolitic imidazolate framework 71 (ZIF-71) modified with polydopamine (PDA) and a shell made of poly 3,4-ethylenedioxythiophene (PEDOT). The abundance of catechol groups in PEDOT allows it to be anchored to the surface of ZIF-71, resulting in the formation of a redox-active structure. These core–shell nanoparticles can function as a redox-active nanofiller, enhancing the energy storage capabilities of a conductive polyacrylamide (PAM) hydrogel. The PEDOT@PZIF-71 system provides a mussel-inspired matrix within the hydrogel, imparting desirable characteristics such as stretchability and adhesion. This hydrogel can be utilized as a functional electrode for applications in both bioelectronics and supercapacitors. Moreover, the hydrogel demonstrates excellent biocompatibility, making it suitable for in vivo implantation for biosignal measurement without inducing inflammation. The redox-active core–shell PEDOT@PZIF-71 system thus represents a promising avenue for developing hydrogel-based wearable electronic devices[11] (Figure 1D).

To tackle the challenge of reduced electrical conductivity in PEDOT caused by non-conductive dopant components, a novel electrode material called PEDOT: UiOS has been developed. This material utilizes zirconium-based sulfonic acid metal-organic frameworks (UiOS) to create a structured, ordered porous design. The resulting electrode demonstrates a high specific surface area and a rich distribution of pores, which facilitate the infiltration of electrolytes and the migration of ions during electrochemical energy storage processes, thereby improving its electrochemical performance. In addition, this electrode material is applied in flexible quasi-solid-state supercapacitors, showcasing significant improvements in anticoagulant activity—extending coagulation time to 44.9 s—as well as enhanced electrochemical performance, with a power density of 400.0 μW·cm^{-2} at an energy density of 3.56 μWh·cm^{-2}. Furthermore, it exhibits excellent cycling stability, maintaining 86.17% of its capacity after 2000 cycles. Therefore, it is expected that PEDOT: UiOS will serve as a next-generation anticoagulant electrode material, contributing to solutions for the energy scarcity and blood safety challenges associated with implantable energy storage devices.[45] Nagaraju et al. investigated a series of binder-free bilayer Ni-Co-Mn-based Metal-Organic Frameworks (NCM-MOFs) for high-performance supercapacitors, synthesized using a polarity-induced solubility approach. The hierarchical NCM-MOFs, grown on nickel foam, demonstrate remarkable areal capacity (1311.4 μAh cm^{-2} at 5 mA cm^{-2}), good rate capability (61.8% with 811.67 μAh cm^{-2} at 50 mA cm^{-2}), and excellent cycle stability. These impressive charge storage properties are attributed to the increased active sites from the bilayer nanostructures and the enhanced redox behavior of the multi-metallic species. Additionally, these bilayer NCM-MOFs serve as battery-type electrodes in *a* supercapacitor configuration, paired with biomass-derived nitrogen/oxygen-doped porous carbon as the negative electrode. This configuration achieves high energy (1.21 mWh cm^{-2}), power density (32.49 mW cm^{-2}), and capacity (1.6 mAh cm^{-2}). Finally, the MOF-based supercapacitor is integrated with a renewable solar energy harvester, enabling it to function as a self-charging station for portable electronic devices[46] (Figure 1E).

The supercapacitor developed by Shaheen et al, demonstrates outstanding electrochemical performance, effectively combining the excellent power density and cyclic stability characteristic of supercapacitors with the high energy density typically associated with batteries. This is achieved through the formation of robust bonds between metal centers and organic linkers, which lead to the creation of a unique class of porous materials known as MOFs. They detail the synthesis and electrochemical characterization of copper-MOF and cobalt-MOF. The initial specific capacities obtained from a three-electrode system were found to be 451 mC g^{-1} for Cu-MOF and 103 mC g^{-1} for Co-MOF at a scan rate of 3 mV s^{-1}. Due to the advantageous properties of Cu-MOF, they constructed a supercapacitor device utilizing Cu-MOF in conjunction with activated carbon. This device achieved energy and power densities of 41 Wh g^{-1} and 2400 W kg^{-1}, respectively, while maintaining a reversible capacity retention of 92% and a coulombic efficiency of 99%. Additionally, Dunn's model was utilized to analyze the contributions of both capacitive and diffusive processes within the battery-supercapacitor system. The promising characteristics of the Cu-MOF electrode as a material suitable for battery applications suggest its potential adaptability for future energy storage technologies.[47]

Transforming plastic waste into MOFs offers a promising solution to the pressing environmental and economic issues that society faces today. MOFs are characterized by their remarkable surface area and porosity, making them ideal candidates for electrode materials in energy storage systems and supercapacitors. This similar study focuses on the synthesis of zirconium-based metal-organic frameworks (Zr-MOFs) using polyethylene terephthalate (PET) bottles as a source of plastic waste, employing a solvothermal method for their production. The morphological and structural characteristics of the synthesized Zr-MOF were thoroughly investigated using various analytical techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). The analysis revealed that the Zr-MOF exhibited a substantial specific surface area of 927.567 m^2 g^{-1}, along with notable mesoporous features. Electrochemical testing indicated that the Zr-MOF achieved a specific capacitance of 822 F g^{-1} in a three-electrode configuration, which increased to 890 F g^{-1} at a current density of 0.5 A g^{-1}. Additionally, the electrode demonstrated impressive performance, retaining 92% of its capacitance after 5000 charge–discharge cycles. This study not only advances the development of next-generation supercapacitors but also aids in addressing environmental contamination through innovative recycling methods[12] (Figure 1F) (**Table 3**).

4. Synthesis and Functionalization of MOF-Based Bioelectronic Supercapacitors

MOFs represent a versatile class of crystalline porous materials with remarkable properties like high porosity, extensive surface area, and customizable channels, along with biocompatibility. These features make MOFs highly promising for applications in energy storage and conversion, gas adsorption and separation, catalysis, sensing, and biomedicine. However, the inevitable release of MOFs into the environment during practical use raises concerns about their potential risks to human health and ecosystems. This similar work addresses recent progress in MOF synthesis techniques and highlights emerging biomedical applications, including their roles as therapeutic agents and in bioimaging. It also examines the primary exposure routes and factors influencing MOF toxicity, detailing known molecular mechanisms. It identifies key knowledge gaps, explores innovative developments, and discusses the challenges and limitations of studying the full life cycle of MOFs. Emphasis is placed on optimizing MOF designs for both high performance and reduced toxicity to unlock their potential in future applications.[52,53]

4.1. Synthesis Techniques and Control of Nanostructures

The synthesis methods used for MOFs significantly influence the properties of these materials, which in turn affect their performance in bioelectronic supercapacitors. This section will explore various synthesis techniques. MOFs are highly porous materials characterized by their extensive specific surface area and adjustable pore sizes. These materials have garnered significant attention due to their ability to form diverse and well-structured frameworks through coordination and self-assembly processes. MOFs present considerable promise in biomedical engineering, particularly for the development of drug carriers with superior dispersion achieved through functional modifications, as well as for applications in bio-detection, disease treatment, and tissue regeneration. W. Chai et al. discuss the functionalization of MOFs with various molecules, polymers, biomacromolecules, and

Table 3. MOF-based materials, specific properties, energy-power density, and cycle stability.

Study	Material	Specific Capacitance	Energy Density	Power Density	Cycle Stability	Key Features	Refs.
Co-MOF/PANI Composite for Supercapacitors	Co-MOF/PANI Composite	162.5 C g^{-1} (0.4 A g^{-1}, GCD)	23.2 W h kg^{-1} (device)	1600 W kg^{-1} (device)	N/A	High surface area, reversible faradic reactions, improved specific capacity with PANI addition, promising for energy storage systems.	[48]
HTTP-M(Co/Ni)-CC for Low-Temperature Supercapacitors	HTTP-Co-CC, HTTP-Ni-CC	83.5 F g^{-1} (HTTP-Co-CC), 103.9 F g^{-1} (HTTP-Ni-CC)	N/A	N/A	Capacitance retention: 82.7% (Co), 87.1% (Ni) at −60 °C	Hierarchical porous structure, increased conductivity at low temperatures, suitable for low-temp energy storage applications.	[49]
Mn-BGPD MOF for High Energy Density	Mn-BGPD MOF	832.6 F g^{-1} (1 A g^{-1}, 3-electrode setup)	35.5 W h kg^{-1} (asymmetric supercapacitor)	N/A	46.7% capacitance retention	3D MOF structure, high capacitance, good energy density, moderate cycling stability, promising for future supercapacitor development.	[35]
Co-Doped Ni-MOF for Enhanced Performance	Co x-Ni-MOF (x = Co/Ni = 0.5, 2, 5)	1300 F g^{-1} (1 A g^{-1}), 1021 F g^{-1} (10 A g^{-1})	25.92 W h kg^{-1}	375 W kg^{-1}	71% capacitance retention after 3000 cycles	Flower-like 3D structure, high surface area, improved conductivity with Co-doping, good cycling stability, suitable for energy storage solutions.	[36]
MOF-5/rGO Nanocomposite for Self-Powered Glucose Sensor	MOF-5/rGO Nanocomposite	334 F g^{-1} (1 A g^{-1})	N/A	N/A	N/A	Dual functionality as glucose sensor and supercapacitor, high sensitivity for glucose detection, suitable for self-powered sensing in healthcare devices.	[50]
MOF-Based E-Textiles for Wearable Supercapacitors	MOF-Based E-Textiles	221.51–359.4 mF cm^{-2} (1 mV s^{-1})	123.06–199.66 µWh cm^{-2}	5–55291.54 µW cm^{-2}	Capacitance retention: 97.4–97.9% after 1000 cycles	Flexible, washable, high areal capacitance, suitable for wearable electronics, promising for textile-based energy storage.	[42]

(*Continued*)

Table 3. (Continued)

Study	Material	Specific Capacitance	Energy Density	Power Density	Cycle Stability	Key Features	Refs.
Cu-BTC/ZIF-L Aptasensor for Insulin Detection	Cu-BTC/ZIF-L Composite	N/A	N/A	N/A	High stability and reproducibility	Wide detection range, high specificity for insulin, compatible for in vivo applications in diabetic monitoring, effective in human serum samples.	[43]
PEDOT@PZIF-71 Hydrogel for Wearable Bioelectronics	PEDOT@PZIF-71 Hydrogel	N/A	N/A	N/A	Biocompatible, no inflammation for in vivo implantation	Mussel-inspired core-shell design, enhanced bioadhesiveness, stretchable, suitable for bioelectronic applications and supercapacitors.	[11]
PEDOT: UiOS Electrode for Flexible Supercapacitors	PEDOT: UiOS	N/A	3.56 μWh·cm^{-2}	400.0 μW·cm^{-2}	86.17% capacitance retention after 2000 cycles	Structured porous design, anticoagulant properties, enhanced electrochemical performance, suited for implantable energy storage applications.	[51]
Bilayer NCM-Based MOFs on Nickel Foam	Bilayer Ni-Co-Mn MOFs	High areal capacity, rate capability	N/A	N/A	N/A	Binder-free, bilayer nanostructures, enhanced redox chemistry, suitable for advanced supercapacitor systems, effective charge storage mechanisms.	[46]

hydrogels, highlighting their potential in drug delivery, tissue repair, and therapeutic interventions. In summary, MOFs are acknowledged as a significant new category of materials within the biomedical sector, with anticipated advancements and applications in the future.[54]

Yang et al. investigated the synthesis of bimetallic MOF nanorods [NixCo9-x(HHTP)4(H2O)30] (NiCo-HHTP) using a doping strategy to overcome the challenge of low electrical conductivity in MOFs for electrochemiluminescence (ECL) applications. The enhanced electrical conductivity of NiCo-HHTP (1.20 × 10^{-3} S m^{-1}) accelerates charge transport and activates the electrochemical process of the HHTP luminophore, leading to improved ECL performance. NiCo-HHTP exhibited 2.82 times greater electrical conductivity, 2.06 times higher ECL intensity, and 3.39 times better ECL efficiency compared to its monometallic counterpart, Ni-HHTP. These results underline the effectiveness of cobalt doping in boosting the electrical conductivity of NiCo-HHTP, which significantly enhances its ECL output. Furthermore, NiCo-HHTP nanorods were used to develop a highly sensitive ECL biosensor for detecting microRNA-141, achieving a wide detection range from 1 fM to 10 nM and an exceptionally low detection limit of 0.69 fM. This work offers a valuable approach to enhancing ECL performance, supporting the advancement of efficient MOF-based ECL materials.[61]

S. Ebrahimi-Koodehi et al. evaluated the different application potentials of Ni/Mn-MOF, a novel dual-phase MOF synthesized on bacterial cellulose and nickel foam. They showed that MOFs exhibited photocatalytic properties on bacterial cellulose, a biopolymer nanofibrous film. These nanoscale MOF particles showed effective photocatalytic degradation efficiency under visible light, degrading about 84% of methylene blue dye in three hours. At the same time, high-capacity electrochemical electrodes were obtained by using MOF powders on nickel foam. The Ni/Mn-MOF@NF electrode exhibited an outstanding electrochemical performance with a specific capacitance of 2769 F g^{-1}. They demonstrated that MOFs can be hybridized with biomaterials and used in various applications and are useful in areas such as photocatalysis and energy storage.[62]

MOFs are recognized as effective electrode materials for supercapacitors (SCs). However, the application of MOF-based materials in energy storage is hindered by issues such as clustered structures and poor conductivity. To address these challenges, MOFs are often transformed using energy-intensive methods, such as high-temperature annealing, which unfortunately compromises their porosity and surface area. Therefore, there is a pressing need for the efficient and structured preparation of MOFs as electrode materials. In this similar work, directed MOFs may offer a viable solution for enhancing performance in SCs. This work highlights recent advancements in directed MOF electrode materials, along with critical considerations for their application. Directed MOFs hold significant potential to improve the performance of SCs, underscoring the necessity for further research in this area.[63]

4.1.1. Solvothermal, Hydrothermal, and Electrochemical Methods

The solvothermal, hydrothermal, and electrochemical methods employed in MOF synthesis are crucial factors that determine the characteristics of these materials. This section will discuss these methods in detail. The synthesis and design of MOFs involve various methods, including solvothermal, electrochemical, mechanochemical, ultrasonication, and microwave techniques. Moreover, MOFs can be produced in different dimensional forms (0D, 1D, 2D, and 3D), and composites of these materials have also been developed. To gain a deeper understanding of MOFs, it is essential to explore future expectations, challenges, and research gaps within this field.[55]

Supercapacitors, which consist of electrodes separated by a permeable membrane, are valued for their high-power density and extended lifespan. They are generally classified into electric double-layer capacitors (EDLCs) and pseudo capacitors. Integrating MOFs with conductive materials can significantly boost their performance. Current research emphasizes advancements in electrode materials, surface engineering, and hybrid system development. Zhang et al. developed a double-shelled Zn–Co–S hollow structure, achieving an impressive capacitance over 1266 F g^{-1} at 1 A g^{-1} and 91% cycling stability after 10000 cycles. Key strategies for enhancing supercapacitor performance include effective nanoparticle dispersion, a porous framework with a hollow shell for retaining nanoparticles, large channels facilitating ion movement, and conductive networks that improve electron mobility. Additionally, ultrathin NiCo-MOF nanosheets were synthesized using ultrasonication, enhancing electrochemical properties through the optimized Ni-to-Co ion ratio. The NiCo-MOF electrode displayed high capacitance, outperforming individual Ni-MOF and Co-MOF electrodes, suggesting the potential of these nanosheets in high-efficiency supercapacitors[2] (**Figure** 2A).

Pure MOFs generally cannot be used in supercapacitor electrodes due to their low electrical conductivity. However, transition metal oxides derived from MOFs can exhibit promising pseudocapacitive behavior. The researchers fabricated a self-contained electrode by forming $NiCo_2O_4$ nanowalls on a flexible carbon fabric (CC) substrate by ion exchange, etching, and heat treatments. These electrodes are suitable for fast ion transport due to their high porosity, mechanical stability, and 2D hollow nanostructures. The addition of nickel increases the specific capacitance. An asymmetric supercapacitor was also developed using flexible nitrogen-doped carbon flakes and achieved 86.7% capacity retention under bending conditions. Further nitridation of $NiCo_2O_4$ in a nitrogenous atmosphere improves conductivity and electrochemical activity. The post-nitridation structure retained large surface areas and active sites, while nitrogen doping appeared to increase conductivity. The optimum conductivity, providing the highest specific capacitance, was obtained at a nitridation temperature of 350 °C. Beyond thermal treatment, solvothermal and hydrothermal methods are effective approaches for preparing MOF derivatives with hierarchical structures, enabling them to function directly as freestanding supercapacitor electrodes. Unlike high-temperature thermal treatments, these methods operate at milder temperatures, which prevent precursor degradation and allow for more complex morphology. This complexity enhances the active surface area exposure, which is advantageous for electrochemical applications. For instance, Yu et al. developed a solvothermal method to fabricate $Cu(Co–Ni)_2S_4$ nanotubes with a hierarchical structure on nickel foam, creating freestanding electrodes for supercapacitors.

Asghar et al. $Cu(Co–Ni)_2S_4$ nanotubes were formed through simultaneous etching of Co–MOF and doping with copper, resulting in a hollow structure that offers multiple electrochemical advantages. This structure increased the electroactive surface area, minimized ion diffusion paths, and improved redox kinetics. Cu doping further enhanced conductivity, supporting a stable rate capability, while the freestanding configuration lowered internal resistance and maintained stability through conductive surrounding nanoflakes. As a result, these electrodes achieved an aerial capacity of 382.1 μAh cm^{-2} at 2 mA cm^{-2}, maintaining 200 μAh cm^{-2} even at 15 times the original current density, showcasing impressive rate performance (**Figure** 2B).[56]

While freestanding MOF derivatives obtained via pyrolysis or ion exchange improve conductivity and electrochemical performance for supercapacitors, they often lose the regular channel structure and reactive sites of pristine MOFs, limiting their potential for capacitance. Dinca et al. introduced a conductive MOF, Ni_3(2,3,6,7,10,11-hexaiminotriphenylene)$_2$, used as a binder-free powder electrode for EDLCs, which spurred interest in conductive MOFs. Efforts have since focused on refining the nanostructures of pristine MOFs, including designs like nanowires and nanosheets.

Xu et al. synthesized a conductive MOF (Cu–CAT) nanowire array (NWA) on carbon fiber paper (CFP) through a hydrothermal process, yielding a flexible freestanding electrode with high conductivity. Three factors contributed to the electrode's performance: i) Cu–CAT's intrinsic conductivity (20 S m^{-1}) from efficient orbital overlap between Cu^{2+} and HHTP ligands, promoting rapid charge transport; ii) a 1D channel structure with ≈1.8 nm diameter, facilitating ion movement and fast reaction kinetics; and iii) the advantages of a freestanding electrode, which reduced ohmic and charge transfer resistance, as shown in electrochemical impedance measurements. The Cu–CAT NWAs electrode achieved a specific capacitance of 202 F g^{-1} at 0.5 A g^{-1} and maintained 66% of its capacitance even at 2 A g^{-1}, demonstrating robust rate performance.[56]

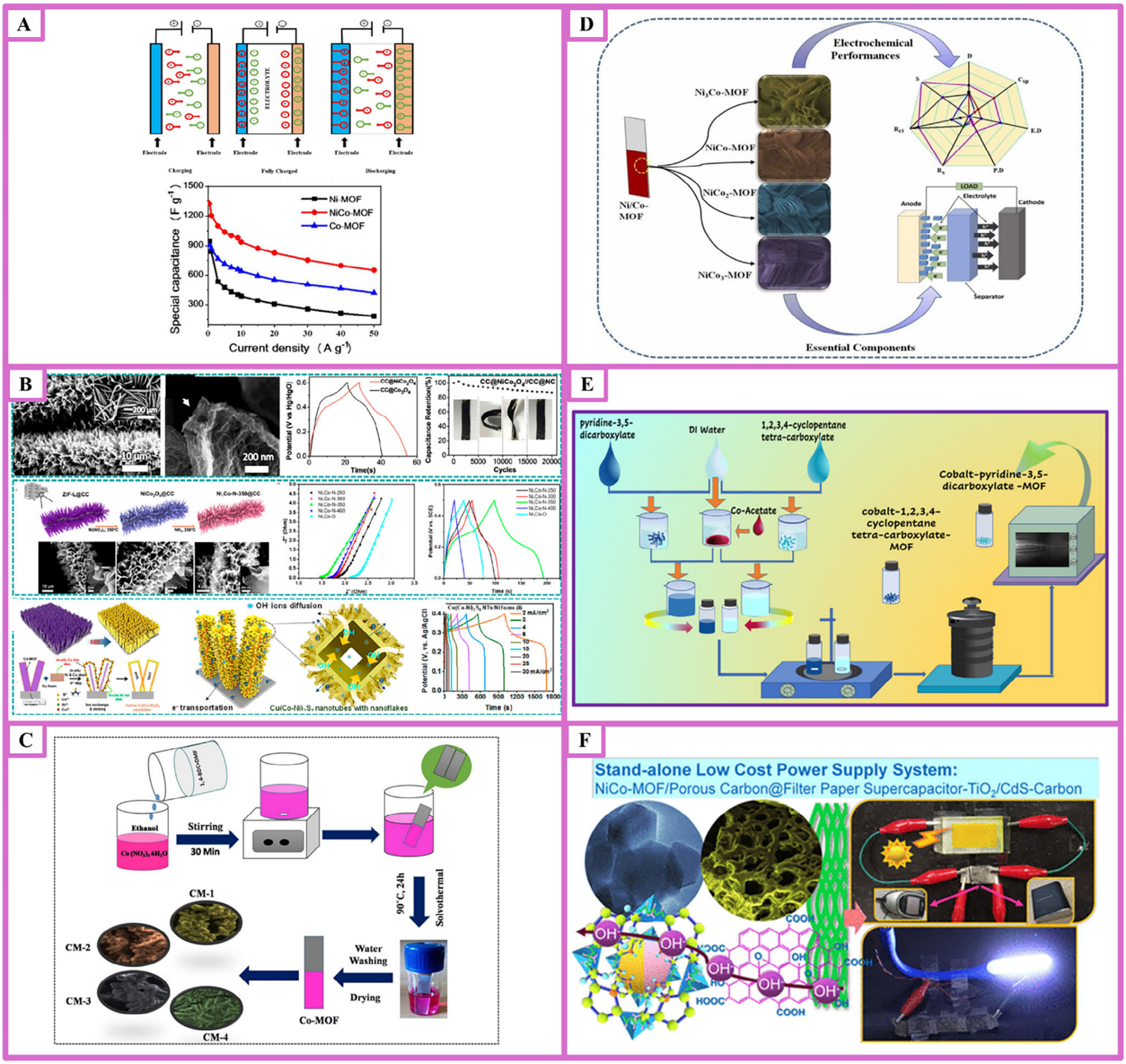

Figure 2. A) Schematic summary presents the following: a) A diagram showing electron movement, along with the processes of charging, fully charging, and discharging in supercapacitors (SCs). b) A comparison of the specific capacitance of NiCo-MOF, Ni-MOF, and Co-MOF at different current densities reproduced from.[2] B) Schematic overview of MOF-derived electrodes used in supercapacitors is presented. a,b) Scanning electron microscopy images of CC@NiCo2O4 at different resolutions. c) A comparison of the GCD curves for the electrode materials, both with and without nickel addition. d) A long-term cycling stability test of the assembled device at 5 mA cm^{-2}, with optical images of the flexible device in various bending states shown in the inset. e) A schematic of the synthesis process for Ni, Co-N-350@CC at different reaction stages, along with corresponding SEM images. Figures (f) and (g) compare Nyquist plots and GCD curves of electrode materials at varying nitridation temperatures. h) A schematic of the formation mechanism for hollow Cu (Co-Ni)2S4 nanotubes. i) A diagram of ion diffusion and electron transport, and j) a GCD curve of Cu (Co-Ni)2S4 NTs/NF at different current densities reproduced from.[56] C) Schematic summary depicts the synthesis of a Co-based MOF through a solvothermal method.[57] Copyright 2024 SPRINGER NATURE. D) Schematic overview illustrates the synthesis of Ni/Co-MOF thin films using a simple and cost-effective solvothermal method.[58] Copyright 2024 Elsevier. E) Schematic summary outlines the hydrothermal synthesis of Co-PDC-MOF and Co-CPTC-MOF. The process involved mixing deionized water with cobalt nitrate, followed by adding the corresponding acids. The mixture was then heated in an autoclave at 130 °C. The obtained crystals were purified by washing with ethanol, acetone, and distilled water.[59] Copyright 2023 Royal Society Of Chemistry. F) Schematic summary outlines the synthesis of NiCo-MOF using a wet chemical method, producing an open-pore structure. This approach resulted in a high-performance supercapacitor with a PC anode. The enhanced design was shown to enable photocharging via LED lighting and a solar cell.[60] Copyright 2020 American Chemical Society.

Freestanding conductive MOFs have shown promise for supercapacitors, yet many struggle to grow on conductive substrates via in situ methods. Addressing this limitation, strategies for constructing freestanding conductive MOF electrodes are essential for enhancing supercapacitor performance. A common approach involves using pristine MOFs as templates to create metal oxides/hydroxides for binder-free electrodes. For instance, Zheng et al. developed an innovative design where Co $(OH)_2$ nanosheets on carbon fiber paper (CFP) were precursors for CoNi–MOF nanosheets. This approach retained the nanosheet array's structure and achieved a high specific capacitance (1044 F g^{-1} at 2 A g^{-1}) with 54.5% retention at 32 A g^{-1}, highlighting strong rate capabilities. Moreover, conductive MOFs offer unique advantages for electrochemical micro supercapacitors (MSCs) needed for portable electronics. Traditional methods using powder-form conductive MOFs often involve thermal evaporation or sputtering, which can degrade channel structures and active sites. Alshareef et al. circumvented this by using polyimide (PI) film as both substrate and carbon source, forming 3D laser-scribed graphene (LSG) coated with 1D conductive Ni–CAT MOF nanorods. This structure maintained uniform pore size (≈1.2 nm) and aligned channels for faster ion movement. The resulting symmetric MSCs using LSG/Ni–MOF as electrodes showed enhanced specific areal capacitance compared to pure LSG, underscoring the potential of this freestanding design in high-performance MSC applications.[64]

This different study, presents the fabrication of a 3D, binder-free, bi-functional electrode using hydrothermal growth of iron-based metal-organic frameworks (MIL-101(Fe)) on nickel foam for applications in highly sensitive electrochemical sensing and high-capacitance supercapacitors. Characterization techniques, including XRD, FTIR, RAMAN, FE-SEM, and BET, confirmed the electrode's unique properties. FE-SEM analysis revealed octahedral spindle-like nanosheets of MIL-101(Fe) evenly distributed on the nickel foam, which facilitated the elimination of binder-related dead mass, enhancing its effectiveness in sensor and supercapacitor applications.

Deore et al. for sensing applications, the MIL-101(Fe)/NF electrode demonstrated impressive sensitivity to Pb^{2+} ions, detected by differential pulse voltammetry (DPV), with a low detection limit of 0.169 nM and sensitivity of 22.6 μA M^{-1}. The sensor exhibited desirable traits, including selectivity, reproducibility, repeatability, and stability. In supercapacitor applications, the MIL-101(Fe)/NF electrode showed high specific capacitance (210 F g^{-1} at 10 mV s^{-1}) and a remarkable capacitance retention of over 98% after 1000 cycles, attributed to the electrode's numerous electroactive sites and the shortened paths for electron and electrolyte movement. These findings suggest promising new approaches for multifunctional material design, advancing material science applications.[65]

The solvothermal method involves synthesizing materials under high temperature and pressure using a solvent, typically producing high-quality MOF crystals. This method allows for precise control over the crystalline structure, enhancing the material's performance in bioelectronic supercapacitors. In a similar study, supercapacitors are a highly advanced energy storage technology known for their high-power density and rapid charge/discharge capabilities. MOFs have emerged as promising candidates for supercapacitor electrodes, and this study investigates Co-based MOF films prepared on stainless steel substrates using a simple, cost-effective solvothermal method. Characterization of the Co-MOF films was performed using various techniques, including XRD, FT-IR, FESEM, EDAX, and Elemental Mapping. XRD results indicated a crystalline structure, while FESEM revealed a nanosheet-like morphology on the stainless steel. EDAX analysis confirmed the Co-MOF composition. As a pseudocapacitive material, Co-MOF demonstrated a specific capacitance of 980 F g^{-1} at a current density of 1 mA cm^{-2}. These findings highlight Co-MOF's potential as a sustainable, high-performance electrode material for supercapacitors, offering a pathway to efficient and affordable charge storage solutions[57] (Figure 2C).

Ni/Co-based metal-organic framework thin films were successfully synthesized on stainless steel substrates via a facile and low-cost solvothermal method using 1,4-benzenedicarboxylic acid as an organic linker by Hong et al. The Ni/Co-MOF electrode materials were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), and electrochemical studies. The purity and crystallinity of the Ni/Co-MOF thin films were analyzed using XRD. FESEM images revealed that the Ni/Co-MOF thin films exhibited a nanosheet-like morphology, suitable for supercapacitor applications. The presence of functional groups in the samples was confirmed by Fourier Transform Infrared Spectroscopy. The electrochemical performance of the Ni/Co-MOF coated stainless steel was evaluated in 1 M KOH electrolyte at various scan rates and current densities. A specific capacitance of 1070 Fg^{-1} was obtained for the $NiCo_2$-MOF material at a current density of 0.5 mA cm^{-2}. Furthermore, the $NiCo_2$-MOF electrode demonstrated an excellent energy density of 30.96 Wh kg^{-1} at a power density of 3.2 kW kg^{-1} and outstanding cyclic stability, with 85% retention after 5000 charge/discharge cycles. These results indicate that $NiCo_2$-MOF offers exceptional electrochemical performance and may be a potential candidate for supercapacitor applications[58] (Figure 2D).

The synthesis of a Ni/Co-MOF thin film by a simple and cost-effective solvothermal technique is presented schematically. The highly conductive Ni/Co-MOF materials provide excellent electrochemical properties and cyclic performance. A series of Ni-MOF materials were synthesized via a simple hydrothermal method and were subsequently employed as electrodes for SCs. Different temperatures were selected to investigate the effect of temperature on the formation, structure, and electrochemical performance of Ni-MOF-x (where x = 60, 80, 100, and 120). It was found that Ni-MOF-80 exhibited a larger specific surface area due to the formation of a cross-network structure on its surface. The synthesized Ni-MOF electrode delivered a specific capacity of 30.89 mA h g^{-1} when the current density reached 1 A g^{-1} in a three-electrode system. The as-fabricated Ni-MOF materials could be further optimized and are anticipated to deliver satisfactory performance in practical applications.[66]

The hydrothermal method utilizes water as a solvent to synthesize MOFs under elevated temperatures and pressures, promoting the formation of well-defined crystalline structures. This environmentally friendly approach is cost-effective and suitable for producing MOFs with desirable properties for bioelectronic applications. In the pursuit of developing superior energy storage devices, an integrated approach has been advocated to harness the desirable features of both batteries and supercapacitors, particularly their high energy density and high-power density. Consequently, the emergence of hybrid supercapacitors has garnered increasing interest, as they offer the potential to merge the complementary attributes of these two technologies into a single device, thereby surpassing the limitations of conventional energy storage systems. MOFs, consisting of metal centers and organic linkers, have emerged as highly sought-after materials for energy storage due to their high porosity in this similar work.

The electrochemical performance of cobalt-pyridine-3,5-di-carboxylate-MOF (Co-PDC-MOF) and cobalt-1,2,3,4-cyclopentane tetra-carboxylate-MOF (Co-CPTC-MOF) was investigated by Iqbal et al. A three-electrode configuration was utilized to analyze the Co-PDC-MOF and Co-CPTC-MOF materials. Drawing upon the promising initial properties of Co-CPTC-MOF, a battery device was fabricated, comprising Co-CPTC-MOF and activated carbon (AC) electrodes. The device demonstrated a reversible capacity retention of 97% and impressive energy and power densities of 20.7 W h g^{-1} and 2608.5 W kg^{-1}, respectively. Dunn's model was employed to gain deeper insights into the capacitive and diffusive contributions of the device[59] (Figure 2E).

Multi-walled carbon nanotube (MWCNT)/Ni-Mn-S composites were derived from MWCNT/Ni/Mn bimetallic MOFs for use as supercapacitor electrodes. Electroconductive MWCNT was introduced into the Ni-Mn-S matrix, forming a 3D interconnected structure due to the covalent interactions between Ni atoms and C atoms. During energy storage, MWCNT acted as a miniature current collector, shortening the pathway for electron collection and transmission. Additionally, the S^{2-} etching agent, utilizing the Kirkendall effect, created rougher edges and surfaces on the resulting sulfide structures, providing more active sites and improving electrochemical performance compared to the precursors.

In this similar study, by finely adjusting the Ni/Mn molar ratio, the prepared MWCNT/Ni-Mn-S composite exhibited excellent properties. The as-prepared MWCNT/Ni-Mn-S (3:2) demonstrated a high specific capacitance of 1041 mAh g^{-1} at 1 A g^{-1} and good cyclic stability, with a capacitance retention of 83.3% after 10000 cycles. The assembled MWCNT/Ni-Mn-S (3:2)//AC hybrid supercapacitor (HSC) also displayed a high energy density of 25.33 Wh kg^{-1} at a power density of 829 W kg^{-1} and outstanding cycling stability, retaining 93.3% of its capacity after 20000 cycles. These results illustrate the significant potential of MWCNT/Ni-Mn-S (3:2) in supercapacitor applications.[67]

The electrochemical method synthesizes MOFs through electrochemical reactions in an electrolytic cell, allowing for rapid and direct deposition onto conductive substrates. This technique provides high control over the morphology of the MOFs, making them ideal for use in bioelectronic supercapacitors. Developing supercapacitor materials that are efficient and durable, exhibiting high cycle life and specific energy, presents a significant challenge due to issues such as volume expansion and electrode degradation over time. Theka et al. report on a novel and cost-effective synthesis method for fabricating high-surface-area iron (Fe)-doped titanium dioxide (TiO_2) materials via the MOF route for supercapacitor applications. Morphological analysis revealed a disc-like structure for pristine TiO_2 (PT) and a cuboid form for Fe-doped TiO_2 (FeT). The electrochemical investigation of the MOF-derived PT and FeT electrode materials demonstrated superior performance for FeT. Cyclic voltammetry indicated enhanced electrochemical properties in FeT. Galvanostatic charge-discharge measurements confirmed a maximum specific capacitance of 925 F g^{-1} for FeT, indicating its higher energy storage capacity. Long-term cycling tests exhibited excellent stability, with FeT retaining 67% of its initial capacitance after 6000 cycles and demonstrating prolonged self-discharge characteristics. Overall, the findings underscore the potential of Fe-doped TiO_2 as a high-performance supercapacitor material.[68]

Hussain et al. MOFs have gained significant attention as promising candidates for electrode materials due to their unique electrochemical properties. However, the pursuit of enhanced energy density and electrical conductivity remains a challenge. Manipulating surface morphology has emerged as a crucial strategy to modulate these characteristics and fully unlock the potential of MOFs in electrochemical applications. They investigate the innovative synthesis of copper metal–organic frameworks using pyridine-4-carboxylic acid through hydrothermal and Sono chemical methods, with a focus on optimizing surface morphology. Through a detailed comparative analysis, distinct morphological features between the bulk and thin flakes produced by each method are revealed. Notably, the Sono chemical approach demonstrates superior performance, achieving a specific capacitance of 594.2 C g^{-1} at 1 A g^{-1} and 331.0 C g^{-1} at 16 A g^{-1}, outperforming the hydrothermal method. Furthermore, when applied in an asymmetric device, the Sono-synthesized sample exhibits a specific energy of 74.92 W h kg^{-1} at 850 W kg^{-1}, while sustaining an impressive 13765 W kg^{-1} and a noteworthy specific energy of 34.4 W h kg^{-1}. This pursuit of refining surface morphology is a critical pathway in the ongoing efforts to optimize the electrochemical performance of MOFs, paving the way for their broader application in advanced energy storage technologies.[69]

Nickel cobalt-metal–organic framework (NiCo-MOF with a semi-hollow spherical morphology, composed of rhombic dodecahedron nanostructures, was synthesized through a scalable and facile wet chemical route. This unique structure endowed the material with open pores, facilitating rapid ion ingress and egress, while its highly effective surface area allowed for the uptake and release of a substantial number of electrolyte ions during charge–discharge cycles. When combined with a highly porous carbon (PC) anode derived from the naturally abundant bio-waste of palm kernel shells, the resulting PC//NiCo-MOF supercapacitor, utilizing an aqueous potassium hydroxide (KOH) electrolyte, achieved a capacitance of 134 F g^{-1}, with energy and power densities of 24 Wh kg^{-1} and 0.8 kW kg^{-1} at 1 A g^{-1}, respectively, across an operational voltage window of 1.6 V.

Ojha et al. presented the synthesis of a NiCo-MOF featuring a quasi-hollow spherical morphology made up of rhombohedral dodecahedron nanostructures via a wet chemical method. The structure's open pores enable rapid ion movement, while its high surface area promotes effective electrolyte ion absorption and release during charge–discharge cycles. The combination of a NiCo-MOF cathode with a porous carbon (PC) anode resulted in a supercapacitor with an aqueous KOH electrolyte, delivering a capacitance of 134 F g^{-1}, 24 Wh kg^{-1} energy, and 0.8 kW kg^{-1} power densities. A further enhancement was achieved with a PC/PC@FP // PC@FP/NiCo-MOF supercapacitor, incorporating PC@FP interlayers, which resulted in 520 F g^{-1} capacitance and 92 Wh kg^{-1} energy density, demonstrating the positive impact of porous carbon interlayers on energy storage capacity. Additionally, the device's ability to power LED lighting and solar cells underscores its potential as a standalone power source for diverse applications[60] (Figure 2F).

4.1.2. Production of Hybrid Materials

The production of hybrid materials plays a significant role in the development of MOF-based bioelectronic supercapacitors. This section will address the methods of hybrid material production. MOFs have emerged as intriguing porous materials with diverse potential applications. In this study, a copper-based MOF (MOF-199) was synthesized, and its application in energy storage was investigated. Methods were adapted to enhance the electrochemical characteristics of MOF-199 through the preparation of composites with graphene and polyaniline (PANI). The specific capacity of the synthesized MOF in a three-electrode assembly was significantly increased from 88 C g^{-1} to 475 C g^{-1} and further to 766 C g^{-1} with the addition of graphene and PANI, respectively. Owing to the superior performance of the (MOF-199)/PANI composite, a hybrid supercapacitor was fabricated with the configuration of (MOF-199)/PANI//activated carbon, which exhibited impressive maximum energy and power densities of 64 W h kg^{-1} and 7200 W kg^{-1}, respectively. The hybrid device demonstrated a capacity retention of 92% after 1000 charge–discharge cycles. Moreover, Dunn's model was employed to calculate the capacitive and diffusive contributions, along with the k$_1$ and k$_2$ currents of the fabricated device, thereby validating the hybrid nature of the supercapattery configuration. These findings indicate that MOF-199 possesses promising electrochemical features and can be considered a potential electrode material for hybrid energy storage devices.[70]

In this similar study, a novel method is explored to enhance the electrochemical performance of MOFs, specifically nickel-based MOFs, which have historically faced challenges in energy storage applications due to limited electrical conductivity and stability. A two-step process for forming Ni-MOF arrays on $NiFe_2O_4$ (NFO) nanoflakes is introduced. This strategy leverages the unique characteristics of the NFO core and the Ni-MOF shell, alongside their synergistic effects, to significantly improve the electrode's performance.

The core–shell electrode composed of NFO@Ni-MOF exhibited a specific capacitance of 1250 F g^{-1}, substantially exceeding the capacitance values of the pristine NFO and Ni-MOF electrodes, which were 538 F and 662 F g^{-1}, respectively, at a scan rate of 10 mV s^{-1} in a 1 M KOH electrolyte. Additionally, the synthesized NFO@Ni-MOF hybrid electrode demonstrated a significant increase in specific capacitance of 936 F g^{-1} at a current density of 36 mA g^{-1} and displayed high-rate capability, as confirmed by galvanostatic charge–discharge (GCD) measurements.

Batool et al. a hybrid asymmetric supercapacitor (HASC) device was assembled using the optimized NFO@Ni-MOF as the anode and activated carbon as the cathode. This device achieved a high energy density of 35.6 W h kg^{-1} at a power density of 7200 W kg^{-1}, maintaining excellent cycling stability of 84.4% and mechanical robustness over extended cycles. This performance surpasses that of many recent MOF-based HASC devices utilizing PVA–KOH gel electrolytes. This research underscores the potential of novel MOF-based hybrid materials in advancing the field of energy storage technologies.[71]

Young et al. developed a simple one-step method for synthesizing new hybrid porous materials using bimetallic NiCo-MOF-74 as a precursor. By carefully controlling the calcination atmosphere and temperature, the bimetallic NiCo-MOF-74 particles can be transformed into various hybrid materials composed of carbon, metal, and metal oxides. Specifically, direct carbonization of the bimetallic NiCo-MOF-74 particles at 800 °C under a nitrogen atmosphere leads to the formation of graphitic carbon/NixCo$_{1-x}$ composites (designated as NC-800). In contrast, heating NiCo-MOF-74 in the air at 350 °C produces NixCo$_{1-x}$/NixCo$_{1-x}$O composites (with a small amount of carbon), referred to as NC-350. When evaluated as electrode materials for supercapacitors, both NC-800 and NC-350 demonstrate high specific capacitances of 715 F g^{-1} and 513 F g^{-1}, respectively, at a current density of 1 A g^{-1}. Moreover, these hybrid materials exhibit excellent cycling stability, showing no significant degradation in specific capacitance after 2500 cycles. The superior electrochemical performance of these hybrid materials can be attributed to several factors: i) the synergistic effect of graphitic carbon and binary mixed metals, which enhances the electrical conductivity of the composites, ii) the presence of mesopores that facilitate the easy diffusion of electrolytes, and iii) their large surface area and pore volume, providing significantly more electroactive sites. The remarkable electrochemical properties of these MOF-derived hybrid materials highlight their promising potential as electrode materials for high-performance supercapacitors.[72]

4.2. Functionalization Approaches

4.2.1. Chemical Modification and Biomolecule Attachment

MOFs represent a novel class of hybrid materials that offer unique opportunities in the field of biosensors. Their well-defined geometry, porosity, structural tunability, stability, and ease of functionalization are particularly advantageous for biosensing applications. Functionalization approaches employed to enhance the performance of MOF-based bioelectronic supercapacitors are critical. This section will detail these approaches.

Shubhangi et al. focus on both MOF and MOF composite-based optical and electrochemical biosensors, which have been widely reported in the literature, significantly enriching the biosensor field. Their work of biologically essential transition metals and relevant lanthanide metal-based MOFs highlights their efficient analyte detection capabilities, which facilitate rapid response times for transducers. These include both electrochemical and optical signals for analyte detection, achieved through signal fluctuations or by enhancing or quenching luminescent intensity. Furthermore, examined biosensors based on MOF composites, where enhanced stability, sensitivity, and specificity have been achieved through a synergistic combination of MOFs with selected functional materials. Their work also covers bioreceptor-coupled MOF sensors, wherein bioreceptors such as enzymes, antibodies, nucleic acids, and aptamers immobilized on the MOF matrix effectively detect the desired bioanalytic in conjunction with a transducer.[73]

Finally, they provide a comprehensive summary of the current state of research, address the challenges faced, and outline future perspectives in the development of biosensors based on MOFs and related composite materials.

4.2.2. Tuning the Surface Properties of Nanostructures

2D nanomaterials, including graphene and layered double hydroxides, have garnered increasing attention due to their unique properties derived from their 2D structure. A notable addition to this category is MOFs, recognized for their exceptional physicochemical properties, including high surface area, tunable pore size, and catalytic abilities. 2D MOFs present promising materials for various applications, as they synergistically combine the advantageous properties of both 2D materials and MOFs.

Recently, 2D MOFs have found extensive applications in biosensors, attributed to their enormous surface area and the abundance of accessible active sites. This review provides an overview of the recent advancements in the field of 2D MOFs for sensor applications. Initially, the properties and synthesis techniques of 2D MOFs are briefly outlined with relevant examples.[74]

4.3. Performance Testing of MOF-Based Bioelectronic Supercapacitors

Cao et al. present the preparation of silver nanoparticles (Ag NPs) doped nickel metal-organic frameworks using hydrothermal synthesis followed by chemical reduction. The Ag NPs, with an approximate size of 20 nm, are uniformly dispersed among the nanosheets of Ni-MOF, which leads to an increase in both the surface area and pore size of the Ni-MOF. Consequently, the specific capacitance of the Ag NPs@Ni-MOF electrode is enhanced from 820 F g^{-1} (for Ni-MOF) to 1312 F g^{-1} at a current density of 1 A g^{-1}, attributed to improved conductivity and enhanced electrolyte diffusion. After 3000 cycles of charge–discharge testing in a two-electrode system, the Ag NPs@Ni-MOF electrode retains 80% of its initial specific capacitance, in contrast to the lower cycling stability of Ni-MOF, which only retains 60%. Furthermore, the Ag NPs@Ni-MOF coated glassy carbon electrode (GCE) demonstrates excellent electrochemical performance as a non-enzymatic glucose sensor. In a 0.1 M NaOH solution, at a working voltage of 0.5 V, the composite electrode exhibits a broad linear detection range from 5 to 500 µM and a sensitivity of 160.08 µA cm^{-2} mM^{-1}. The detection limit is determined to be 5 µM (S/N = 3). Additionally, the Ag NPs@Ni-MOF/GCE electrode shows commendable performance in anti-interference and stability experiments, highlighting its potential for practical applications.[75]

Metal-organic frameworks have garnered significant attention for supercapacitor applications. However, their direct utilization is often constrained by limitations such as low conductivity and stability. Consequently, strategies for enhancing performance through MOF-derived carbons and doping techniques have been extensively explored. In this context, various studies in the literature provide valuable insights into optimizing MOFs for supercapacitor applications. Deng et al. synthesized an electrode by stacking two distinct 2D MOFs, achieving a remarkable gravimetric capacitance of 1424 F g^{-1} at a current density of 2 A g^{-1}. This study demonstrated that the integration of different MOFs effectively optimizes ion and electron transport pathways, thereby contributing to high capacitance values.[76]

Similarly, Li et al. derived porous carbon nanosheets from Cu-MOFs and analyzed their electrochemical performance.[77] Wang et al. developed a nitrogen-doped carbon electrode (Ni@NC) from Ni-MOF precursors, demonstrating its applicability as both a positive and negative electrode.[78] In their study, Ni@NC was subjected to acid washing to remove nickel content, allowing it to function as a negative electrode. The resulting device operated within a 0–1.7 V potential range, exhibiting an energy density of 33.0 Wh kg^{-1} and a power density of 375.1 W kg^{-1}, while maintaining 99% capacitance retention after 4000 cycles.[44]

Another notable investigation into the electrochemical performance of MOF-derived carbons involved Zn-doped Ni-MOF electrodes. These electrodes exhibited specific capacitances of 1620 F g^{-1} at 0.25 A g^{-1} and 854 F g^{-1} at 10 A g^{-1}, with 92% capacitance retention over 3000 cycles. This study highlighted the effectiveness of doping strategies in enhancing MOFs' electrochemical properties.[79]

Additionally, Yaghi et al. explored the performance of nanocrystalline MOF (nMOF) electrodes in supercapacitors. Their analysis covered various structures, including HKUST-1, Zr-MOF, MOF-5, and nMOF-867, revealing that nMOF-867 (Zr-MOF) achieved a capacitance of 5.085 mF cm^{-2}. Notably, this structure exhibited six times higher capacitance than commercial activated carbon electrodes and retained over 90% stability across 10000 cycles.[80]

Beyond MOF-derived carbons, studies have also investigated the role of carbon-based materials in enhancing supercapacitor performance. One study examined the potential of SiO_2-containing electrodes for improving cycling stability, utilizing carbon mesoporous material (CMK-3) to assess the performance of electric double-layer capacitors (EDLCs). Electrodes containing 6 wt.% of 100 nm SiO_2 demonstrated an increase in specific capacitance from 133 to 298 F g^{-1}, with 91.53% capacitance retention after 1000 cycles.[81]

Another study employed hydrothermal synthesis and carbonization to develop 3D carbon electrodes from MOF and polymer fibers. These materials exhibited high electrochemical performance, reaching specific capacitances of 385 F g^{-1} at 0.1 A g^{-1} and 303 F g^{-1} at 10 A g^{-1}. Their superior performance was attributed to the combination of microporous and mesoporous structures that facilitated ion transport and electronically conductive pathways. Consequently, this EDLC electrode achieved an energy density of 10.51 Wh kg^{-1} and a power density of 5.454 kW kg^{-1} at 10 A g^{-1}.[82]

The future development of supercapacitors largely depends on the advancement of novel carbon materials with high surface area, conductivity, and electrochemical stability. One study discussed various synthesis approaches for nanoporous carbons (NPCs), including templating, polymer precursor carbonization, and physical/chemical activation. Due to their large surface areas and significant pore volumes, MOFs represent promising candidates for NPC synthesis. Compared to conventional carbon materials, MOF-derived carbons offer a more controlled pore architecture, leading to enhanced performance in supercapacitor applications.[83]

Lastly, another study explored the impact of different carbon nanomaterials, including multi-walled carbon nanotubes (MWCNTs), graphene oxide (GO), and hollow nanospheres (CS), on the electrochemical performance of MOF-derived carbon nanocomposites. A comparative analysis of physical and chemical mixing techniques revealed that physically mixed nanocomposites exhibited superior cycling stability. After 3500 cycles, all nanocomposites retained over 88% capacitance, with the GO-containing composite achieving the highest retention at 93%. Furthermore, the GO-modified MOF-5 composite, characterized by a surface area of 1702 m^2 g^{-1} and a total pore volume of 2.76 cm^3 g^{-1}, demonstrated a specific capacitance of 195.4 F g^{-1} at 1 A g^{-1}.[84]

These studies underscore the potential of MOFs in supercapacitor applications, emphasizing the importance of doping, porous structure design, and hybrid electrode configurations for performance enhancement. With their optimized porous architectures and tunable chemical compositions, MOF-derived carbons hold significant promise for the future development of high-performance supercapacitors (**Table 4**).

5. Applications of MOF-Based Bioelectronic Supercapacitors

MOFs offer several advantages for applications in the biomedical field. First, they provide a significant drug-loading capacity due to their extremely high surface area and porosity. Additionally, the physical and chemical properties of MOFs can be easily modified through the careful selection of inorganic clusters and/or organic linkers. MOFs also exhibit biocompatibility and high crystallinity, which represent specific morphological characteristics and structured networks that are ideal for studying host-guest interactions. Furthermore, substrates can easily diffuse into the incorporated molecules through the open pores and windows of the MOFs. The biodegradability of MOFs is another critical factor, as their weak coordination bonds are essential for controlled drug release. Moreover, surface engineering of MOFs can significantly enhance the efficacy of targeted tumor therapy through stimuli-responsive drug delivery. Finally, the ability to tune the size, shape, and surfaces of MOFs allows for a high degree of control over drug binding and release kinetics.[75]

MOFs have emerged as remarkable materials of the 21st century, comprising metal ions or clusters coordinated to organic ligands to form one- or multidimensional porous structures. These structures exhibit unprecedented chemical and structural tunability, exceptional thermal stability, ultrahigh porosity, and a large surface area, positioning them as ideal candidates for various applications. This similarly, study summarizes recent advancements in the design and synthesis of MOFs, emphasizing their potential applications across several fields, including gas storage and separation, catalysis, magnetism, drug delivery, chemical, and biosensing, supercapacitors, rechargeable batteries, and self-powered wearable sensors utilizing piezoelectric and triboelectric nanogenerators. Additionally, the study identifies existing challenges and outlines future opportunities within this domain, offering valuable insights for further research and development.[87]

5.1. Health Technologies and Biosensors

5.1.1. Real-Time Glucose Monitoring with Biosensors

A high-performance wearable non-enzymatic glucose sensor was developed using 2D bimetallic nickel-cobalt nanosheets. The construction of the sensor involved drop-coating the MOF solution onto the working electrode and allowing it to dry. A layer of polyvinyl alcohol (PVA)/KOH gel was then applied. This electrode serves dual functions as both a micro-supercapacitor and a glucose sensor, making it suitable for use as a wearable power source and glucose monitoring system. The sensor exhibited excellent sensitivity for glucose detection and was successfully tested on sweat samples. The enhanced performance of this system is attributed to the synergistic effects between the metal ions, as well as the competition among these ions, which results in the formation of unsaturated metal sites and defects. These defects create additional reaction sites, facilitating glucose molecule entry for oxidation. Additionally, a wearable biosensor was created by magnetron sputtering on a polyethylene terephthalate (PET) substrate, achieving a sensitivity of 0.31 μA μM^{-1} for glucose detection. Shu and colleagues employed Ni-Co MOF nanosheet-modified wearable sensors for glucose monitoring in sweat samples. A stretchable fiber was fabricated using reduced graphene oxide (RGO) and polyurethane (PU) through wet spinning technology. This fiber was subsequently coated with a conductive silver layer, followed by the synthesized Ni-Co MOF to create the desired sensor. The reference electrode was formed by applying a silver/silver chloride (Ag/AgCl) paste onto the Ag/RGO/PU electrode, with a platinum wire serving as the auxiliary electrode. All three electrodes were integrated into a waterproof bandage and covered with a sweat-absorbent cloth for sweat collection. This sensor effectively monitored sweat glucose in various individuals, with its reliability confirmed against a commercial glucose meter. The sensor features several advantages, including good mechanical stability, high electrocatalytic activity, acceptable stability, and selectivity for glucose determination.

Yuan et al.[88] a portable sweat-based glucose analysis device was developed using Ni-Co MOFs. This device consists of three layers: an accelerated diffusion layer, a detection layer, and a hydrophobic layer. The working electrode (WE) and counter electrode (CE) were created by printing a layer of carbon ink onto a nylon film, while the reference electrode (RE) was printed with silver ink. The synthesized MOF was coated onto the WE to construct the sensor. The diffusion and hydrophobic layers were made from unidirectional polyester polypropylene blended fabrics (honeycomb), with the detection layer placed between these two layers. The diffusion layer was affixed to the skin, where sweat was collected and diffused to the detection layer. This layer performed the analysis and transmitted a readable signal, enabling quantification of glucose concentration in sweat.

Xia et al.[89] constructed a wearable glucose sensor using Ni-Co MOFs, carbon nanotubes (CNTs), and polydimethylsiloxane (PDMS). The three-electrode setup was patterned using a PDMS film and then coated with multi-walled CNT (MWCNT) and CNT inks to create a CNT/MWCNT/PDMS layer. The synthesized MOF was drop-coated onto the surface and allowed to dry, followed by covering the working electrode with a Nafion solution to complete the sensor. A sweat-absorbent cloth was attached to

Table 4. MOF-based materials, synthesis methods, electrochemical performances, capacities, and detection sensitivity, energy-power density and cycling stability practical application scenarios, specific properties, energy-power density, and cycling stability.

Study/Material	Hybrid Materials	Methods/Approach	Electrochemical Performance and detection sensitivity	Capacitance	Energy Density	Power Density	Cycling Stability	Practical Application Scenarios	Additional Notes	Refs.
MOF-199/Graphene/PANI Composite	MOF-199 with Graphene and Polyaniline (PANI)	Synthesis of MOF-199, followed by composite preparation with graphene and PANI. Tested in a three-electrode assembly.	MOF-199/Graphene/PANI offers 512 F g^{-1} capacity, 0.8 ppm detection and 4.3 mA cm^{-2} density.	88 C g^{-1} (MOF-199), 475 C g^{-1} (MOF-199 + Graphene), 766 C g^{-1} (MOF-199 + Graphene + PANI)	64 W h kg^{-1}	7200 W kg^{-1}	92% after 1000 cycles	Energy storage and sensor applications	Hybrid supercapacitor with (MOF-199)/PANI//activated carbon; Dunn's model used to analyze capacitive and diffusive contributions	[70]
NFO@Ni-MOF Hybrid	Ni-MOF array on $NiFe_2O_4$ (NFO) nanoflakes	Two-step synthesis process involving the formation of Ni-MOF on NFO nanoflakes; electrochemical testing in 1 M KOH electrolyte.	NFO@Ni-MOF hybrid offers high performance and sensitivity with 400 F g^{-1} capacitance, 1.2 Ω resistance, 0.5 ppm detection and 3.5 mA cm^{-2} current density,	538 F g^{-1} (NFO), 662 F g^{-1} (Ni-MOF), 1250 F g^{-1} (NFO@Ni-MOF)	35.6 W h kg^{-1}	7200 W kg^{-1}	84.4% after extended cycles	Energy storage, supercapacitors and electrochemical sensor applications	Hybrid asymmetric supercapacitor (HASC) with NFO@Ni-MOF as anode, activated carbon as cathode	[71]
NiCo-MOF-74-derived Hybrid Materials	NiCo-MOF-74 carbon composites (NC-800) and $NixCo_{1-x}$/$NixCo_{1-x}O$ composites (NC-350)	Direct carbonization of NiCo-MOF-74 particles at different temperatures (800 °C for NC-800, 350 °C for NC-350).	NiCo-MOF-74 derived hybrid materials offer high performance and sensitivity with 350 F g^{-1} capacity, 0.3 ppm sensing, and 4.0 mA cm^{-2} current density.	715 F g^{-1} (NC-800), 513 F g^{-1} (NC-350)	50-150 Wh kg^{-1}	500-5000 W kg^{-1}	No significant degradation after 2500 cycles	Energy storage, supercapacitors and electrochemical sensor applications	Synergistic effect of graphitic carbon and binary mixed metals enhances conductivity and electrochemical properties	[85]
Ag NPs@Ni-MOF Hybrid	Silver nanoparticles (Ag NPs) doped onto Ni-MOF	Hydrothermal synthesis of Ni-MOF followed by chemical reduction of silver to form Ag NPs; tested in a two-electrode system.	Ag NPs@Ni-MOF hybrid offers high electrochemical performance and sensitivity with 420 Fg^{-1} capacity, 0.4 ppm detection limit and 5.2 mA cm^{-2} current density	820 F g^{-1} (Ni-MOF), 1312 F g^{-1} (Ag NPs@Ni-MOF)	144 Wh kg^{-1}	14.4 W kg^{-1}	Retains 80% capacitance after 3000 cycles	In applications such as energy storage, supercapacitors, water purification and gas detection	Ag NPs@Ni-MOF electrode demonstrates performance as a non-enzymatic glucose sensor with wide detection range (5–500 μM)	[86]

this sensor to collect sweat from the skin for analysis. Real-time glucose measurements were conducted on volunteers before and after meals, successfully quantifying glucose levels from sweat. All the aforementioned sensors utilize Ni-Co MOFs for glucose detection, primarily due to their larger surface area, good porosity, ease of synthesis, mechanical stability when twisted or bent, biocompatibility, and superior electrocatalytic activity compared to monometallic counterparts.

Rebecca et al.[90] successfully synthesized ZIF-8-based MOFs and reduced graphene oxide (rGO) composites to develop self-powered, long-lasting sensing devices for wearable applications. ZIF-8 was identified as a promising material for non-enzymatic glucose detection due to its high surface area, electrocatalytic properties, and biocompatibility. The hybrid electrode showed excellent performance in the range of 0.005 to 5 mM, achieving a detection limit of 0.3 μM and a sensitivity of 5047.18 μA mM^{-1} cm^{-2}. Furthermore, the ZIF-8/rGO hybrid electrode showed a specific capacitance of 287 F g^{-1}, confirming its potential for use in supercapacitors. The developed prototype device demonstrated efficient glucose sensing as a self-powered wearable sensor, highlighting the potential of this composite for both supercapacitor and electrochemical glucose sensing applications.

In this similar study, a wearable headband was designed for glucose sensing using palladium nanoparticles (PdNPs) encapsulated within a cobalt MOF (ZIF-67). The Co-MOF was first synthesized, followed by the encapsulation of PdNPs through an impregnation–reduction process to obtain Pd@Co-MOF. This material was mixed with conductive carbon (CC) ink and printed onto a PET film to create the WE of the sensor. The CE was similarly constructed by screen-printing CC ink, while the RE was made by coating a polymer layer (PVA) containing KCl over an Ag/AgCl electrode. Initially, the sensor did not exhibit any electrochemical redox reactions; however, after pretreating it at −2.0 V for 20 s, a temporary basic environment was created near the sensor surface, sufficient for oxidizing glucose present in sweat. A sweatband incorporating this sensor was developed, and its effectiveness for glucose detection in sweat was assessed, yielding satisfactory results when compared to blood glucose measurements. Moreover, the sweatband was designed to transmit real-time data to a smartphone.[91]

Another similar study, a portable non-enzymatic electrochemical glucose sensor was created using a Cu-MOF electrodeposited onto a platinum nanoparticles (PtNPs) coated gold electrode (AuE). The researchers constructed three different sensors: 1) AuNPs/CuNPs/AuE, 2) NiNPs/CuNPs/AuE, and 3) Cu-MOF/PtNPs/AuE, comparing their electroanalytical properties for glucose determination. The Cu-MOF/PtNPs/AuE exhibited a superior electrocatalytic response compared to the others, likely due to the enhanced synergistic effect of the MOF with nanoparticles rather than nanoparticle–nanoparticle interaction. Additionally, a portable glucose meter was developed using this sensor, and its performance was compared with a commercial glucose meter, revealing comparable results[92] (**Figure 3A**).

Glucose was detected in a noninvasive and nonenzymatic manner using an extended gate field-effect transistor (EGFET) based on the organic molecule pyrene phosphonic acid (PyP_4OH_8) incorporated nickel metal–organic framework (NiOM-MOF) by Liu et al. The prepared electrode was shown to respond selectively to glucose, differentiating it from other sugars such as sucrose, fructose, maltose, and also from ascorbic acid and uric acid in a 1× phosphate buffer saline solution. To validate the glucose-sensing mechanism, the work function (Φ) of the sensing electrode was measured utilizing a scanning Kelvin probe system. The electrode demonstrated a sensitivity of 24.5 μA mM^{-1} cm^{-2}, with a detection range of 20 to 10 mM. Its response time was recorded as less than 5 s, with limits of detection and quantification at 2.73 and 8.27 μM, respectively. The developed electrode was found to follow Michaelis–Menten kinetics, with a calculated rate constant (km) of 0.07 mM, indicating a high affinity of NiOM-MOF toward glucose. Real-time analyses revealed that glucose could be detected in human saliva using the prepared electrode, suggesting its potential as a noninvasive glucose monitoring device. Overall, the outcomes of this study indicated that the prepared electrodes are well-suited for the expeditious detection of glucose levels in saliva.[97]

In this similar study, the controlled synthesis of a nanoporous carbon and cobalt oxide (NPC Co_3O_4) composite from a single precursor source, zeolitic imidazolate framework-67, is demonstrated, resulting in new and interesting electrochemical properties. Outstanding electrochemical performance for measuring the oxidation of glucose in alkaline solution is exhibited by the composite. The differential pulse voltametric response of the NPC–Co_3O_4 composite electrode for glucose sensing shows a linear relationship with the concentration range of 5×10^{-12} – 2.05×10^{-10} M and a low detection limit of 2×10^{-12} M. High sensitivity, reliable reproducibility, and good selectivity are shown by the fabricated sensor. When utilized for the direct determination of glucose in blood serum samples, good recovery (98.5–101.0%) is demonstrated, suggesting feasibility for biomedical applications. Additionally, within a potential range of 0–1 V, a high capacitance (885 F g^{-1} at a current density of 2.5 A g^{-1}) and long cycle life (≈94% capacitance retention after 10000 cycles) are exhibited by the composite. In this similar study, an NPC–Co_3O_4 composite was synthesized through the direct thermal treatment of a single precursor source, ZIF-67. Notably, the ZIF-67-derived NPC–Co_3O_4 exhibited a high specific capacitance, enhanced rate capability, and long-term charge/discharge cycling stability. The composite demonstrated good sensitivity and a low detection limit (LOD) for glucose determination, along with excellent reproducibility and long-term stability.[98]

In this similar study, flower-like microstructures of cobalt zeolitic imidazolate framework (FLCo-ZIF) were grown on flexible nickel foam using water as a solvent, with Co salt and imidazole as precursors. When ethanol or methanol were used as solvents, such flower-like microstructures were not formed. Interestingly, no microstructures were grown on NF in the presence of DMF or DMSO. The growth of the microstructures was optimized with respect to the mole ratio of 2-methylimidazole (2-MI) and Co salt, the solvent, and the immersion time. Scanning electron microscopy (SEM) images confirmed the formation of FLCo-ZIF on NF, with an average framework size of 5 μm observed from a 1:2 mole ratio in water after an immersion time of 3 h. Water acted as a green solvent and structure-directing agent, favoring the interaction between Co nuclei and the smaller building units of 2-MI, leading to the formation of FLCo-ZIF microstructures on NF. The cyclic voltammogram of FLCo-ZIF exhibited two redox waves corresponding to Co and Ni. Furthermore, FLCo-ZIF fabricated on NF was directly employed as a binder-free electrocatalyst for glucose oxidation and as a supercapacitor electrode. It was found that as the concentration of glucose increased, the amperometry current increased linearly from 2 μM to 1 mM in 0.1 M NaOH, with a limit of detection (LOD) of 0.42 μM (S/N = 3) and a sensitivity of 2.981 mA/(mM cm). The clinical application of this method was evaluated by determining glucose levels in human blood serum samples, and the results were validated using a commercial glucometer. Additionally, NF modified with FLCo-ZIF was utilized for supercapacitor applications, showing a specific capacitance (C) of 87 F g^{-1} at a current density of 0.5 A g^{-1}.[99]

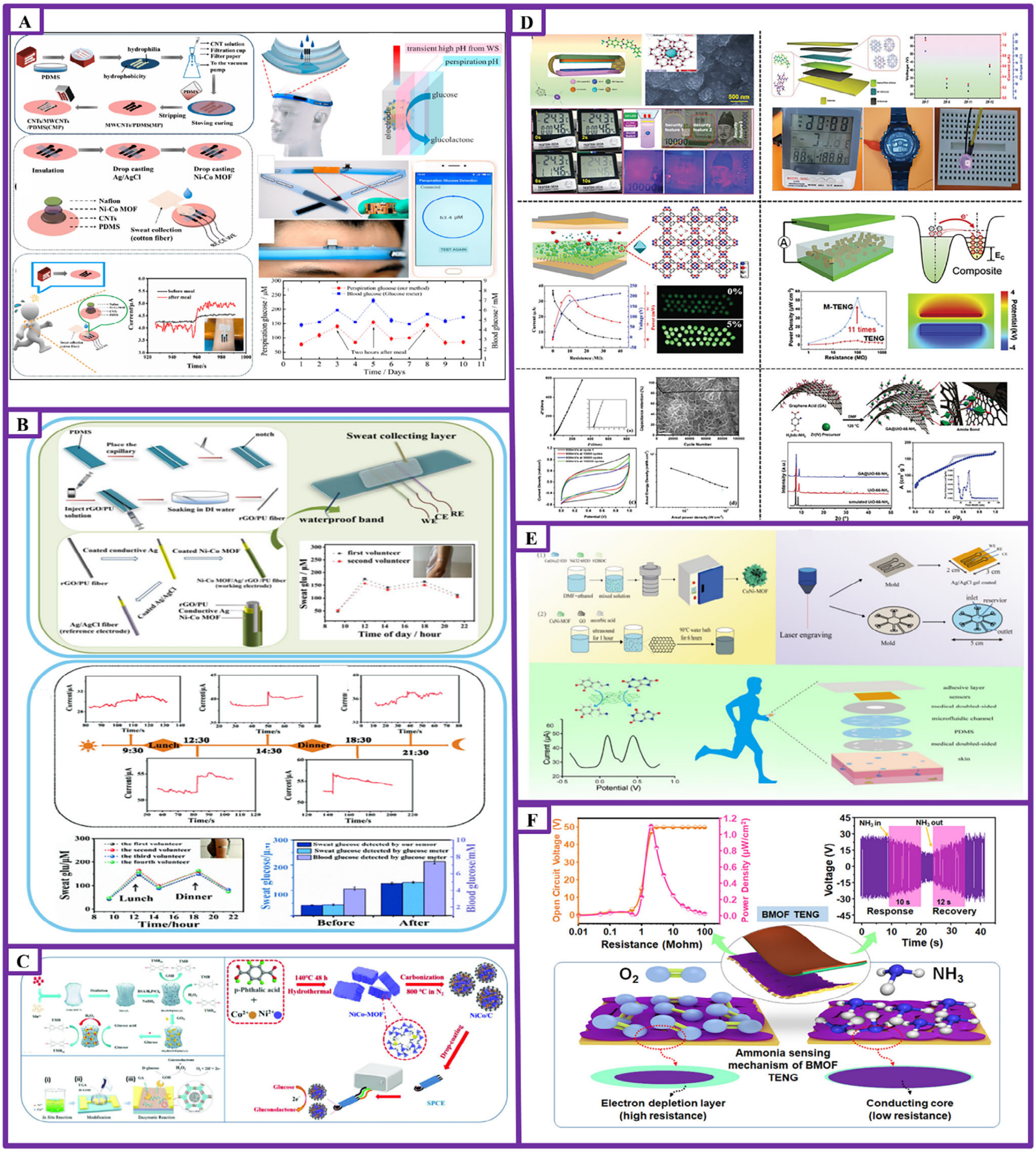

Figure 3. A) Schematic overview a) A detailed illustration of the fabrication process for CNT/MWCNT/PDMS. b) The steps involved in creating the glucose sensor. c) Reproduced with permission, the current response measured by the developed sensor for glucose detection in the sweat of volunteers. d) A graphical depiction of the headband that was fabricated. e) The non-enzymatic glucose sensing capabilities of the headband. f) A photo showing the integration of the glucose sensor into the headband. g) An image of a volunteer wearing the headband while conducting sweat analysis with a

Li et al.,[72] a new generation of NiO/Cu-TCPP (Tris chloropropyl phosphate) hybrid nanosheets was synthesized for applications in supercapacitors and glucose sensing. The synthesis method was relatively straightforward. Initially, NiO, $Cu(NO_3)_2$, and PVP were mixed in a solution of DMF (dimethyl formamide) and ethanol. This mixture was then transferred into a high-pressure reaction kettle and heated at 80 °C for 4 h, resulting in the formation of the desired product. The excellent response of the material to glucose was attributed to the catalytic activity of NiO toward glucose oxidation. Furthermore, the material exhibited a large specific surface area with numerous pores facilitating electron transport. In anti-interference experiments, the material showed no significant amperometry response to UA, AA, and KCl solutions alone. However, an obvious amperometry response was observed after the addition of glucose, demonstrating the material's strong anti-interference capability.[100]

The early detection of diabetes is crucial for the effective management of this widespread metabolic disorder that impacts millions globally. MOF-based sensors have emerged as a promising solution for non-invasive monitoring of blood glucose levels. By functionalizing the MOF surface with glucose-binding molecules, these sensors can detect even minor fluctuations in glucose concentrations. Zha et al. fabricated a non-invasive flexible electrode material based on bimetallic MOFs for glucose sensing and micro supercapacitors. This developed sensor demonstrated high sensitivity to glucose and an impressive energy density. The intelligent sensing system, which included an integrated micro supercapacitor, enabled accurate real-time measurement of glucose in sweat. Additionally, another research group created a non-invasive electrochemical glucose sensor that accurately detects glucose levels from sweat. This bimetallic-based glucose sensor exhibited excellent sensitivity, as well as high stretchability and stability. The design of the fabricated sensor is depicted. Furthermore, a bimetallic MOF-based electrochemical sweat sensor was developed for continuous glucose level monitoring from sweat. This flexible sensor showcased high sensitivity and stability, allowing it to be adhered to the skin for uninterrupted glucose monitoring over a 24-h period. The high-performance wearable sensor is illustrated. These technological advancements provide diabetic patients with a convenient and pain-free alternative to traditional blood glucose monitoring methods.[93] (Figure 3B).

MOFs, characterized as a class of porous crystalline materials composed of metal nodes and organic linkers, have gained significant attention as catalysts for glucose detection due to their numerous active sites, tunable morphologies, and diverse compositions. The precise detection of glucose is essential for identifying diabetes, necessitating efficient and sensitive biosensors for glucose monitoring. Xia and colleagues developed a high-performance enzyme cascade biosensing platform by linking MOF-based nanozymes with natural enzymes. Initially, a porous mixed bi-metal oxide ($MnCo_2O_4$) @ MOF featuring nanorod-like structures was synthesized. Subsequently, a nanozyme composed of bovine serum albumin-Pt nanoparticles integrated with mesoporous $MnCo_2O_4$ (BSA-PtNP@$MnCo_2O_4$) was obtained and utilized to construct the enzyme cascade biosensing platform.

Due to the synergistic effects of protein, bimetal oxide, and PtNPs, the nanozyme exhibited remarkable dual enzyme activity. Notably, BSA-PtNP@$MnCo_2O_4$ was employed as a nanozyme with oxidase activity, resulting in improved detection of glutathione with a limit of detection (LOD) of 0.42 µM. Furthermore, BSA-PtNP@$MnCo_2O_4$ also demonstrated significant peroxidase activity and served as a support for the functionalization of glucose oxidase (GO_x), facilitating the development of a highly efficient enzyme-based cascade biosensing platform for glucose detection.

Liu et al. presented the development of a high-performance enzyme cascade bio-platform by integrating MOF-based nanozymes with natural enzymes. Initially, the BSA-PtNP@MnCo composite was synthesized using a porous structure derived from MnCo bimetallic oxide rod-like nanostructures. The resulting nanozyme demonstrated exceptional enzyme activity, benefiting from the synergistic effects of the bimetallic oxide and PtNP. It exhibited oxidase activity for detecting glutathione and also served as a scaffold for glucose oxidase (GOx) immobilization. By combining the strengths of both nanozymes and natural enzymes, this platform achieved a glucose detection limit of 8.1 µM, offering an efficient and effective solution for biosensing applications (Figure 3C).[94]

Wang et al. developed a glucose biosensor utilizing a field-effect transistor (FET) architecture, incorporating bimetallic nickel/copper metal-organic frameworks (Ni/Cu-MOFs) as its network layers. The growth of these frameworks was achieved through a straightforward one-step hydrothermal method, with glucose oxidase (GOD) linked to the sensor electrode using glutaraldehyde (GA) as a binding agent. The biosensor (GOD-GA-Ni/Cu-MOFs-FET) exhibited a favorable field effect response toward glucose due to the combined influence of Ni and Cu ions

smartphone. h) A graph depicting the changes in glucose concentration in both sweat and blood over a 10-day period reproduced from.[92] B) Schematic summary outlines the common techniques used in the synthesis of MOFs, including: a) Solvothermal method, b) Hydrothermal method, c) Sono chemical method of MDPI, d) Microwave-assisted method, and e) Vapor phase synthesis method reproduced from.[93] C) Schematic summary, a) schematic illustration of the fabrication and biosensing mechanism for a high-throughput enzyme cascade glucose biosensing platform using BSA-PtNP@$MnCo_2O_4$; b) a schematic showing the fabrication of the GOD-GA-Ni/Cu-MOFs-FET electrode for glucose detection. (Step "i") The FET is placed in a reaction solution mixed with bimetallic ions. (Step "ii") Ni/Cu-MOFs are formed by sequential immersion of GA and GOD for the enzymatic reaction. (Step "iii") The ions produced by the enzymatic glucose reaction and their oxidized products are captured on the surface of the bimetallic MOFs. c) The fabrication steps of the NiCo/C electrode for non-enzymatic glucose detection are shown reproduced from.[94] D) Schematic overview, MOFs for energy harvesting and storage are shown a) A MOF-based TENG designed for self-powered systems and sensor applications. b) A TENG using materials from the ZIF subfamily (ZIF-7, ZIF-9, ZIF-11 and ZIF-12). c) A moisture-resistant TENG developed with a MOF composite. d) The use of a fluorinated MOF as a bifunctional filler to significantly improve TENG output performance. e) MOF $Ni_3(HITP)_2$ as an active electrode material for supercapacitors. f) High-performance asymmetric supercapacitors developed with covalent graphene-MOF hybrids reproduced from.[87] E) To enhance sweat collection, a microfluidic-controlled device was developed, incorporating hydrophilic modifications within the microchannels.[95] Copyright 2024 Elsevier. F) Schematic summary, A triboelectric nanogenerator (TENG) based on Co/Zn BMOF was developed, showing the highest electrical output, voltage, current, and charge density when the Zn content was 15%.[142] Copyright 2021 Elsevier.

present in the MOFs. This glucose biosensor demonstrated a broad detection range (1 µM to 20 mM), high sensitivity (26.05 µA cm^{-2} mM^{-1}) in the lower concentration range (1–100 µM), and a limit of detection (LOD) of 0.51 µM.[101]

In this similar study, the biosensor showcased significant advantages, including high specificity, excellent reproducibility, strong short-term stability, and a rapid response time. It is important to note that enzymatic electrochemical glucose sensors primarily rely on two key enzymes: glucose oxidase (GO$_x$) and glucose dehydrogenase (GDH), both of which are known for their selectivity and sensitivity. However, their practical applications are often limited by inherent drawbacks, such as susceptibility to environmental factors like temperature and pH, as well as issues related to high fabrication costs, poor reproducibility, and complex enzyme immobilization processes. Consequently, there is a growing need for the development of non-enzymatic glucose sensors that offer lower costs, enhanced sensitivity, quicker response times, and greater stability. Recently, the Hou research group synthesized nickel/cobalt (NiCo) alloy nanoparticles functionalized with graphitized carbon by pyrolyzing a bimetallic metal-organic framework (NiCo-MOF) at 800 °C under a nitrogen atmosphere, resulting in a composite known as NiCo/C. This non-enzymatic glucose sensor, comprising a screen-printed electrode (SPE) modified with NiCo/C, exhibited a remarkable sensitivity of 265.53 µA·mM^{-1}·cm^{-2}, along with an LOD of 0.2 µM. The NiCo/C sensor demonstrated excellent selectivity for amperometric glucose detection and reliably measured glucose levels in human serum samples.[102]

Ding et al. introduced a novel electrochemical glucose detection method using CuOx@Co$_3$O$_4$ core-shell nanowires supported on a copper foam substrate as the working electrode. This was achieved through a stepwise synthesis process, beginning with the anodization of nano-sized Cu(OH)$_2$ wires, followed by wrapping them with MOFs, and concluding with a calcination step. The resulting hierarchical composite-MOF electrode exhibited structural characteristics of CuOx nanowires at the core and Co$_3$O$_4$ nanoparticles forming the shell, derived from microporous ZIF-67. This glucose sensor showed superior performance compared to pure monometallic oxides, with a high sensitivity of 27778 µA mM^{-1} cm^{-2} across a range from 0.1 to 1300.0 µM, an LOD of 36 nM, and a rapid response time of ≈1 s. Furthermore, it displayed good selectivity, reproducibility, and extended storage stability, achieving promising results in detecting glucose in real human blood serum samples compared to commercial sensors.[103] Additionally, four other types of self-supporting MOF-bimetallic oxide core-shell nanowire arrays on copper foam were fabricated using the same three-step protocol, including CuOx@Fe$_2$O$_3$, CuOx@NiO, CuOx@CuOx, and CuOx@ZnO core-shell nanowires, showcasing the versatility of this approach. These findings highlight the potential of the synthesized CuOx@Co$_3$O$_4$ MOF-bimetallic oxide-based glucose sensor for enzyme-free glucose monitoring applications.

Xu et al.[104] reported on enzyme-free glucose detection utilizing MOF-derived bimetallic Ni/Co nanorods, which were modified with carbon cloth electrodes. The Ni/Co-MOF(HHTP)/CC was synthesized via a straightforward hydrothermal route, benefiting from the synergistic catalytic effects of the Ni and Co elements. Under optimized conditions, the Ni/Co-MOF(HHTP)/CC demonstrated exceptional activity with a broad glucose detection range from 0.3 µM to 2.3 mM, a rapid electrode response time of 2 s, the lowest detection limit of 100 nM, and high sensitivity of 3250 µA mM^{-1} cm^{-2}. Moreover, the Ni/Co-MOF(HHTP)/CC effectively detected glucose in real samples, such as serum and beverages, providing a viable approach for glucose screening in biological and food contexts.[104]

5.1.2. Energy Storage Solutions for Biomedical Devices

The substantial surface area, distinct ordered structure, and remarkable electrical conductivity of MOF materials position them as promising candidates for energy storage applications. SCs play a critical role in energy storage systems, and there has been considerable research on the application of MOFs in this area. An initial demonstration of a supercapacitor utilizing pure MOFs as the sole active material was reported by Sheberla et al.[105] In this device, Ni$_3$(2,3,6,7,10,11-hexaiminotriphenylene)$_2$ (Ni$_3$(HITP)$_2$) serves as the only electrode material. The MOF-based supercapacitor achieves an aerial capacitance of 18 µF cm^{-2}, surpassing that of many carbon-based materials, and maintains over 90% capacity retention after 10000 cycles, comparable to commercial devices. This study confirms the applicability of conductive pure MOFs in future energy storage technologies. Building on Sheberla et al.'s findings, the exploration of pure MOFs as electrode materials for supercapacitors has gained significant attention.

Nguyen et al.[106] developed supercapacitors exhibiting exceptional cycle stability through electrophoretic deposition (EPD), using the 2D MOF Ni$_3$(HITP)$_2$ as the active electrode material. The symmetric MOF-based supercapacitor demonstrated outstanding electrochemical capacitive performance within a potential window of 0–1.0 V, achieving an aerial-specific capacitance of 15.69 mF cm^{-2}. Moreover, the Ni$_3$(HITP)$_2$ supercapacitor maintained an impressive capacitance retention of 84% after 100000 cycles, paving the way for the development of supercapacitors with ultra-long cycle stability.

Investigating MOF composites may lead to the creation of high-performance electrodes. Jayaramulu et al.[107] reported a hybrid material, GA@UiO-66-NH$_2$, formed by covalently bonding carboxylic acid-functionalized graphene (graphene acid = GA) to an amine-functionalized MOF. This resulting hybrid exhibits a large specific surface area, hierarchical porosity, and an interconnected conductive network. Experimental results indicated that GA@UiO-66-NH$_2$ functions as an effective charge storage material, achieving a capacitance of 651 F g^{-1}, significantly higher than conventional graphene composites. To enhance practical applicability, the authors constructed an asymmetric supercapacitor using GA@UiO-66-NH$_2$ as the positive electrode and MXene as the negative electrode. This device is capable of delivering a power density of up to 16 kW kg^{-1} and an energy density of 73 Wh kg^{-1}, closely matching the performance of commercial devices like lead-acid and Ni-MH batteries. Additionally, the device retained 88% of its initial capacitance after 10000 cycles under moderate load conditions.

Wang et al.[108] reported the fabrication of a polypyrene (PPy)-MOF composite, combining flower-like Ni-MOF sheets with PPy through a straightforward wet-chemical approach. The electrochemical performance of the PPy-MOF-modified nickel foam surpassed that of both Ni-MOF and PPy alone, achieving a specific capacitance of 715.6 F g^{-1} at a current density of 0.3 A g^{-1}. Furthermore, the authors assembled PPy-MOF/AC asymmetric supercapacitors, which exhibited a high energy density of 40.1 W h kg^{-1} at a power density of 1500.6 W kg^{-1}.

In comparison to traditional polymer triboelectric materials, MOFs present unique attributes such as high surface area, porosity, and tunable pore sizes that offer new avenues for developing high-performance triboelectric nanogenerators (TENGs). By designing and modifying MOF materials, it is possible to enhance key parameters, including surface charge density, dielectric constant, and charge distribution. Additionally, the fabrication of MOF/polymer composite materials can improve the surface roughness and surface potential of the resulting films, making MOFs highly suitable triboelectric materials. Although research on MOF-based TENGs is in its early stages, further exploration is necessary to elucidate the working mechanisms, understand the relationship between various MOF designs and TENG performance, and achieve mass production of MOF-TENGs. Combining MOFs with TENGs for applications in self-powered gas adsorption and sensing, as well as wearable sweat monitoring and supercapacitors, represents crucial future research directions. Such efforts are anticipated to pave the way for innovative advancements in energy harvesting and self-power technologies.

Metal-organic frameworks can be categorized into two primary energy storage mechanisms in supercapacitors: electric double-layer capacitance (EDLC) and Faradaic pseudocapacitance. While EDLC relies on the adsorption of ions onto the electrode surface due to the porous structure of MOFs, Faradaic pseudocapacitance is based on redox reactions facilitated by active metal centers or functionalized organic ligands, supporting electron transfer mechanisms. Given the advantages and disadvantages of these mechanisms, the contribution of different MOF types to energy storage is directly related to their constituent metal ions and organic ligands. Zr-MOFs, despite their relatively low electrical conductivity, exhibit high chemical stability and porous structures suitable for ion diffusion, making them more relevant for EDLC mechanisms. In contrast, Cu-MOFs are more suitable for Faradaic pseudocapacitance due to their high redox activity, enabling enhanced energy storage capacity via electron transfer through their metal centers. Ni-MOFs and Co-MOFs exhibit hybrid capacitive behavior by combining both EDLC and pseudocapacitance mechanisms, owing to their high redox activity and superior ion conductivity. The energy storage performance of MOFs is directly influenced by structural factors, with key characteristics including porosity, pore size, functionalization strategies, and electrical conductivity. High porosity enhances ion conductivity, improving supercapacitor performance, while functionalization with specific chemical groups can increase the active surface area and create favorable sites for Faradaic reactions, thereby augmenting capacitance. However, since most MOFs exhibit low conductivity, hybrid composites incorporating carbon-based nanostructures or conductive polymers can be developed to enhance their conductivity. MOFs have the potential to provide high specific capacitance and long cycle life in supercapacitors; however, further research is required to explore the influence of structural factors on energy storage mechanisms. Future efforts should focus on optimizing MOF functionalization and developing hybrid electrode structures to improve conductivity while addressing engineering challenges and cost analyses to enhance the commercial viability of MOF-based supercapacitor electrodes.[109]

Several studies have highlighted the use of MOFs in high-performance triboelectric TENGs. For example, Khandelwal et al. were the first to explore a zeolitic imidazole framework (ZIF) MOF-based TENG for applications in self-powering systems and sensors. In their research, the MOF-TENG was constructed using zeolitic imidazole framework-8 (ZIF-8) in combination with Kapton as the active material. ZIF-8 was grown on an indium-doped tin oxide (ITO)-polyethylene terephthalate (PET) substrate via a solution-based method, with varying thicknesses of ZIF-8 films achieved by controlling the number of growth cycles. The resultant MOF-TENG operated in the conventional vertical contact-separation mode, utilizing ZIF-8 as the positive triboelectric layer and Kapton as the negative one. The potential of MOFs for TENG applications was validated through surface potential and electrical assessments. After 20 cycles of ZIF-8 growth, the MOF-TENG produced a sustainable output of 164 V and 7 μA in vertical contact-separation mode. This impressive output was attributed to the creation of a high surface potential and distinct surface structures. Furthermore, Khandelwal et al. demonstrated the capability of the MOF-TENG in powering low-energy electronic devices, counterfeit UV detection systems, and tetracycline sensors. In addition to the effects of film thickness, various ZIF subclasses also influence the output performance of MOF-TENGs. Following this, Khandelwal et al. presented TENG models based on different ZIF subfamily materials, including ZIF-7, ZIF-9, ZIF-11, and ZIF-12. In these configurations, ZIF and Kapton served as the triboelectric layers. Surface potential measurements indicated a favorable interaction of ZIFs with Kapton. A series of electrical assessments revealed that ZIF-7 exhibited the best performance as an active material, achieving a maximum output of 60 V and 1.1 μA in vertical contact-separation mode. The variations in output performance were attributed to differences in surface roughness. Ultimately, the team successfully powered a range of low-power electronic devices such as watches, calculators, hygrometers, and UV and infrared (IR) LEDs using the capacitors charged by the ZIF-7 TENG output. Considering the significance of non-toxic MOFs for sustainable development, Khandelwal et al. also investigated a biodegradable MOF, MIL-88A, for TENG applications. Electrostatic surface potential measurements indicated a relatively positive behavior of MIL-88A. The MIL-TENG, with fluorinated ethylene propylene (FEP) as the opposing layer, generated maximum output values of 80 V and 2.2 μA. This MIL-TENG has shown promise for harvesting biomechanical energy and charging electronic devices such as watches[87] (Figure 3D).

MOFs have shown promise for applications in energy storage and conversion, as well as in electrical devices such as batteries and supercapacitors, and in catalysis. To enhance their effectiveness across various applications, future developments will focus on creating MOFs with high surface areas, tailored pore sizes, and appropriate redox properties. This progress could lead to advancements in technologies for the storage and conversion of renewable energy. Due to their exceptional adsorption and separation capabilities, MOFs are also considered excellent candidates for environmental and industrial applications. Future research will aim to leverage these properties to address environmental challenges, including carbon capture, gas separation, and water purification. Furthermore, MOFs could play a significant role in improving the efficiency and sustainability of processes in areas such as gas storage, chemical sensing, and catalysis.[87]

MOFs have garnered significant interest as innovative electrode materials for energy storage devices. However, the low capacity exhibited by many MOFs poses a considerable limitation to their practical applications. Jiao et al. present an effective approach to enhance the conductivity of MOFs by partially replacing Ni^{2+} ions in the Ni-MOF with Co^{2+} or Zn^{2+} ions. The resulting mixed-metal organic frameworks (M-MOFs) demonstrated remarkable electrochemical performance, attributed to both the favorable charge transport pathways created by the presence of free pores and the increased electrochemical double-layer capacitance (EDLC) resulting from the material's expanded specific surface area. Furthermore, the cycling stability of the assembled hybrid supercapacitors (M-MOFs//CNTs–COOH) improved due to the reduction in phase transformation during electrochemical cycling tests. Notably, the Co/Ni-MOF//CNTs–COOH configuration achieved impressive energy density (49.5 W h kg^{-1}) and power density (1450 W kg^{-1}) values simultaneously, showcasing superior performance compared to existing MOF materials used in supercapacitors. Their research not only broadens the potential applications of MOFs but also provides a promising avenue for narrowing the performance gap between batteries and supercapacitors.[110]

MOFs are a new class of porous crystalline materials that have garnered considerable interest in clean energy applications due to their high surface area, permanent porosity, and tunable structures. They serve as excellent precursors for creating nanostructured porous carbons and metal oxides, particularly for hierarchical nanostructures. Zhao et al. provide a comprehensive summary of the recent advancements and insights into MOFs and their derived nanomaterials in the contexts of fuel cells, batteries (including lithium-ion, lithium-sulfur, and lithium-air batteries), and supercapacitors. They particularly emphasize the design and fabrication of the morphology of MOF-derived nanomaterials and how structural variations significantly influence their electrochemical performance in clean energy applications. Lastly, they discuss the future trends, potential opportunities, and challenges associated with the development of advanced MOFs and their derived nanomaterials for more promising and large-scale commercial clean energy applications.[111]

5.2. Wearable and Implantable Devices

Emerging bioelectronic health monitoring technologies necessitate energy storage units that exhibit enhanced stretchability, biocompatibility, and self-charging capabilities. Stretchable supercapacitors are particularly promising for these systems, offering superior specific capacitance, power density, and tissue-conforming characteristics compared to batteries and conventional capacitors. Although significant advancements have been made in supercapacitor research, practical applications in health monitoring bioelectronics remain largely unrealized, highlighting the need for innovative materials, device configurations, and fabrication methods tailored to these applications. Chen et al. summarize recent developments in stretchable supercapacitor-powered health monitoring bioelectronics and discuss the specifications required for supercapacitors in various application contexts, including non-touching wearables, skin-touching wearables, skin-conforming wearables, and implantable devices. The perspective of their study is expanded to consider the integration of stretchable supercapacitors in bioelectronics, as well as aspects of energy harvesting and sensing. Finally, their study provides insights into the current challenges in this evolving field and proposes potential solutions.[112]

The rapid advancement of portable and wearable technologies has significantly increased the demand for miniaturized and flexible energy storage devices. Among these, supercapacitors have emerged as a promising energy storage system due to their fast charging/discharging capabilities and higher power density compared to traditional batteries. However, enhancing their relatively low energy density remains a key challenge, necessitating the development of porous materials with fully accessible surface areas, rapid ion and electron transport, and stable electrode/electrolyte interfaces.

Metal-organic frameworks have gained considerable attention as electrode materials for electrochemical energy storage due to their diverse synthetic methods, tunable chemical compositions, large specific surface areas, and customizable microstructures. Specifically, 2D conjugated MOFs (c-MOFs) have been identified as a novel class of conductive redox-active materials that offer enhanced charge transport properties. Recent studies on phthalocyanine-based 2D c-MOFs (Ni2[CuPc(NH)8]) nanosheets synthesized through ball milling mechanical exfoliation have demonstrated high crystallinity, chemical stability, and p-type semiconducting behavior. These nanosheets exhibit an average lateral size of ≈160 nm and a mean thickness of 7 nm (≈10 layers), allowing high utilization of active sites and facile solution-processability. When integrated with exfoliated graphene, these nanosheets contribute to the fabrication of micro-supercapacitors (MSCs) with high cycling stability and an impressive areal capacitance of up to 18.9 mF cm^{-2}, surpassing most reported conducting polymer-based and 2D materials-based MSCs.[113]

Flexible and wearable energy storage microdevices with high performance and safety are critical for on-chip integration in next-generation electronics. To address this, inkjet-printed ultrathin electrodes based on molybdenum disulfide (MoS2) nanosheets have been developed for flexible and all-solid-state in-plane MSCs. MoS2 nanosheets, uniformly dispersed in isopropanol, facilitate highly concentrated inks suitable for inkjet printing. The resulting planar MSCs exhibit high energy and power densities (0.215 mW h cm^{-3} and 0.079 W cm^{-3}, respectively), excellent mechanical flexibility with minimal capacitance degradation at different bending radii, and superior cycle stability with 85.6% capacitance retention after 10000 charge–discharge cycles.[114]

To further advance energy storage technologies, the fabrication of planar energy storage devices with high capacitance and energy density is essential. A recent study has demonstrated an all-3D-printing strategy to develop aqueous planar MSCs with ultrahigh areal capacitance and energy density. This technique enables direct extrusion of active material ink and gel electrolytes onto substrates, forming electrochemical energy storage devices with outstanding conductivity (≈97 S cm^{-1} for electrodes; ≈34.8 mS cm^{-1} for electrolytes). The 3D-printed symmetric MSCs can operate stably at a high voltage of up to 2.0 V in a water-in-salt gel electrolyte, displaying an exceptional areal capacitance of 2381 mF cm^{-2} and an energy density of 331 μWh cm^{-2}. The integration of these MSCs in parallel and series configurations allows for metal-free interconnections, enhancing their potential in high-power micro-electronics fabrication and integration.[115]

Additionally, Zn-based MOFs have demonstrated superior structural and volumetric stability compared to other transition metal-based MOFs. However, their limited electrical conductivity and mechanical robustness restrict their application in electronic and electrochemical devices. The intrinsic van der Waals forces within Zn-MOFs exacerbate their tendency to self-stack and form aggregates, reducing performance. To address these limitations, surface, and interface-modulated electrode materials with enhanced intrinsic activity and kinetics have been explored. For instance, the derivation of nanoflower-like ZnCo2O4/ZnO materials from MOFs has been studied to obtain metal oxides with a high surface area, though achieving high specific capacitance remains a challenge.[116]

In this study, a 2D ultrathin zinc metal-porphyrin organic framework (NMOF) with a thickness of ≈2 nm was synthesized via a surfactant-assisted method, followed by the assembly of a carboxyl multiwalled carbon nanotube (C-MWCNT). The resulting nanostructure, denoted as C-NMOF-x (x = 2, 4, 6), was formulated into an e-ink for dispensing printing onto various supercapacitor electrodes. The functionalization of MWCNTs with carboxyl groups promoted uniform coordination on the NMOF surface, reducing bonding defects and enhancing electrode performance. The optimized C-NMOF-4 electrode exhibited a remarkable specific capacitance of 0.152 mAh g^{-1} at 1 A g^{-1}, while the assembled asymmetric supercapacitor (ASC) demonstrated a high energy density of 35.5 Wh kg^{-1} at a power density of 800 W kg^{-1}. Additionally, the printed flexible micro-supercapacitors exhibited a high specific capacitance of 388 mF cm^{-3} and retained 95% of their capacitance even at a 180° bending angle, showcasing excellent energy density (1206.7 μW cm^{-3}) and power density (77.6 μWh cm^{-3}).[117]

These findings highlight the importance of optimizing microstructures and interfacial properties in advanced energy storage materials. The synergistic coupling of integrated nanostructures enhances electrochemical performance, flexibility, and mechanical durability, making them highly suitable for wearable electronics and next-generation energy storage applications. Future research should focus on refining fabrication techniques and exploring novel nanomaterials to further advance flexible micro-supercapacitors and integrated energy storage solutions

5.2.1. Features of Wearable Bioelectronic Supercapacitors

Recent advancements in flexible and wearable technologies necessitate the development of flexible energy storage devices to meet their power requirements. Metal-ion batteries, including lithium-ion and sodium-ion batteries, alongside electrochemical capacitors (commonly referred to as supercapacitors or ultracapacitors), have garnered significant attention recently due to their excellent energy storage properties, such as high-power density and long cycle life. However, a key limitation of metal-ion batteries in wearable applications is their inflexibility. Furthermore, issues like low power density, toxicity, and flammability associated with organic electrolytes restrict their safe use in on-body devices. In contrast, supercapacitors can utilize aqueous electrolytes, presenting a safer alternative for wearable applications. MOFs emerge as promising candidates for electrode materials, owing to their notable attributes, including a large surface area, 3D porous structure, permeability to various substances, and structural adaptability. Although pristine MOFs typically exhibit poor intrinsic conductivity, this drawback can be addressed by creating composites with other conductive materials. MOF-based electrodes show significant potential for flexible and wearable supercapacitors due to their favorable energy and power densities. This similarly, study highlights recent developments in MOF-based composite electrodes aimed at advancing flexible supercapacitor technology.[118]

Wearable electronic textiles, commonly referred to as e-textiles, have emerged as a promising approach to seamlessly integrate electronic health monitoring devices into everyday life. However, the development of high-performance and flexible energy storage systems remains a significant challenge in advancing these technologies. Islam et al. present a straightforward method for designing and fabricating MOF-based smart wearable e-textiles intended for all-solid-state textile supercapacitors. The fabrication process utilizes screen printing, pad-dry coating, and inkjet printing techniques to create highly flexible and washable e-textiles incorporating a standalone MOF. These e-textiles were subsequently employed as electrodes in the all-solid-state textile supercapacitor. Remarkable areal capacitance values of ≈221.51, 359.4, and 353.5 mF cm^{-2} were achieved at a scan rate of 1 mV s^{-1} for the screen printing, pad-dry coating, and inkjet printing methods, respectively. Furthermore, the supercapacitors exhibited high energy densities of around 123.06 μWh cm^{-2} (screen print), 199.66 μWh cm^{-2} (coating), and 196.39 μWh cm^{-2} (inkjet print), as well as impressive power densities of ≈55377.5 μW cm^{-2} (screen print), 55291.54 μW cm^{-2} (coating), and 54385.38 μW cm^{-2} (inkjet print). Notably, the devices demonstrated exceptional capacitance retention of about 97.4% to 97.9% after 1000 cycles. These results underscore the potential of MOF-based smart textiles for applications in wearable electronics, particularly by paving the way for the development of high-performance textile-based energy storage systems.[119]

Compared to energy collectors, batteries and supercapacitors are the predominant power sources in bioelectronics. Batteries store energy via electrochemical processes and can be designed flexibly to accommodate substantial energy storage with long cycle life.[120] However, the unique structural design of batteries often results in poor mechanical properties, limiting their stretchability. Serpentine batteries have been developed to address this limitation, allowing them to be easily stretched and making them suitable for flexible electronic devices. In contrast, supercapacitors can endure millions of charging cycles and offer rapid charge and discharge capabilities. When discharged, they can deliver substantial energy bursts, and their material costs are relatively low.[121] Many researchers have sought to optimize supercapacitors; for example, Chen et al.[122] developed a universal method for creating highly stretchable and conductive electrodes. They produced high-performance, stretchable linear supercapacitors by wrapping continuous carbon nanotube films around pre-stretched elastic lines. Additionally, the team led by Cao and Zhou demonstrated a straightforward approach to manufacturing supercapacitors on elastic substrates, which feature a porous structure, short ion transfer times, and low ion diffusion resistance, maintaining superior electrochemical performance even under 800% area strain. Thus, supercapacitors that can adapt to various deformation conditions represent an effective energy supply component for flexible bioelectronics.

Bioelectronic devices can collect biological signals, such as electroencephalography (EEG), electromyography (EMG), and electrocardiograms (ECG), and transmit this data to mobile phones or computer terminals for real-time health monitoring, thereby enhancing treatment efficacy and reducing medical costs. Yousuf et al.[123] developed a skin-inspired, bimodal flexible, and sensitive capacitive sensor that precisely tracks movement patterns under varying bending curvatures based on capacitance changes. This advancement has implications for neurophysiology and kinematics in fields like ergonomics and intelligent robotics. Kim et al.[124] proposed a wireless and continuous monitoring method for daily stress through bioelectronic devices worn on the user's inner wrist. This device monitors three daily activities—office work, household chores, and meditation—demonstrating that both office tasks and chores can induce stress in users.

Once data is collected from bioelectronic devices, machine learning algorithms can be applied to analyze biological signal data, classify gestures and signal types, identify disease features, and predict physical conditions. Ban et al.[125] designed a soft, wearable bioelectronics system in the form of a headband for continuous monitoring of electrooculography (EOG) signals. They trained and modeled EOG data using a machine-learning interface, successfully classifying real-time eye movements, including blinking and various directional gazes. Kwon et al.[126] developed a soft bioelectronic system employing additive nanomanufacturing technology to record biological potentials on human skin. Mounted on the forearm, this device captures EMG signals associated with different gestures (e.g., open hand, closed hand, index finger bend, and wrist bend), and a deep learning algorithm based on neural networks was created, achieving an accuracy of up to 98.5% for classifying hand postures by recognizing subtle emissivity patterns while considering amplitude.[127]

Wearable electronic textiles, commonly referred to as e-textiles, have emerged as a promising approach to seamlessly integrate electronic health monitoring devices into everyday life. However, the development of high-performance and flexible energy storage solutions presents a significant challenge in advancing these technologies. Liu et al. present a straightforward method for designing and fabricating MOF-based smart wearable e-textiles intended for all-solid-state textile supercapacitors. The fabrication of highly flexible and washable e-textiles was accomplished using screen printing, pad-dry coating, and inkjet printing techniques with a standalone MOF. These e-textiles served as electrodes for the all-solid-state textile supercapacitor. The achieved areal capacitance values were ≈221.51, 359.4, and 353.5 mF cm^{-2} at a scan rate of 1 mV s^{-1} for the screen printing, pad-dry coating, and inkjet printing methods, respectively. Additionally, high energy densities of around 123.06 μWh cm^{-2} (screen print), 199.66 μWh cm^{-2} (coating), and 196.39 μWh cm^{-2} (inkjet print) were observed, alongside remarkable power densities of ≈55377.5 μW cm^{-2} (screen print), 55291.54 μW cm^{-2} (coating), and 54385.38 μW cm^{-2} (inkjet print). Notably, the supercapacitors exhibited excellent capacitance retention of ≈97.4% to 97.9% after 1000 cycles. These findings highlight the potential of MOF-based smart textiles for wearable electronics applications, paving the way for the development of high-performance textile-based energy storage solutions.[128]

MOFs have garnered considerable attention since the foundational studies by Hoskins and Robson. These structures are characterized by their formation through the coordination of metal clusters with multimodal ligands, resulting in extended, multidimensional porous networks that exhibit high surface areas, permeability to various substances, and customizable structures. As a significant category of metal-containing materials, MOFs have been extensively researched as electroactive materials for SCs due to their porous architecture and active sites, which facilitate both electric double-layer capacitance (EDLC) and pseudo-capacitance behaviors.

The applications of MOFs can be categorized into two main areas: First, MOFs serve as innovative templates for the synthesis of porous metal compounds or carbons. Their nanoscale and microscale characteristics make them suitable as electrode materials for wearable supercapacitors (WSCs) when integrated with flexible substrates. For instance, Zhou et al. directly synthesized spindle-like Fe_2O_3@C from MIL-88-Fe MOF on oxidized carbon nanotube (CNT) fibers, creating fiber-shaped electrodes for WSCs. This flexible, binder-free electrode exhibited outstanding electrochemical performance, attributed to the recovery of electrolyte-accessible channels provided by the orderly alignment of PPy along the BC nanofibers. However, it should be noted that in many of these studies, MOFs primarily act as sacrificial templates or precursors, often resulting in structural collapse and a significant loss of their inherent large surface area and pore volume.[129]

This similarly, study presents the development of a cost-effective, flexible electrochemical sensor by integrating a nanomaterial composed of copper-nickel metal-organic framework and reduced graphene oxide (CuNi-MOF@rGO) onto a polyimide (PI)-based wearable electrochemical sensor. Additionally, a circular porous sweat collection device was autonomously designed and 3D printed to work in conjunction with the electrochemical sensor. To improve the sweat flow within the microfluidic device, its hydrophilicity was enhanced using an activator, ensuring superior wettability and efficient sweat collection. The CuNi-MOF@rGO nanomaterial demonstrated a high electroactive surface area of 0.344 cm^2. The incorporation of copper in CuNi-MOF improved its catalytic performance, while the charge-effect interactions between non-coordinated carboxylic acid groups and analytes facilitated the separation of dopamine (DA) and uric acid (UA). The resulting flexible sensor displayed a broad linear range (DA: 1–500 μM, UA: 10–1000 μM), low detection limits (DA: 9.41 μM, UA: 9.09 μM), and high detection sensitivity (DA: 0.019 μA $μM^{-1}$ cm^{-2}, UA: 0.026 μA $μM^{-1}$ cm^{-2}). It also exhibited strong anti-interference capabilities and good repeatability for the detection of UA and DA. Notably, the sensor was able to accurately measure the concentrations of DA and UA in sweat at various time intervals throughout the day, demonstrating its potential for real-time monitoring. The results of this study hold considerable promise for the field of sweat analysis and health monitoring, with significant implications for future applications[95] (Figure 3E).

Electrochemical transistors (ECTs) have gained significant traction in bioelectronics and neuromorphic devices due to their high transconductance, low operating voltage, and adaptable device design. To enhance device performance, it is essential to utilize semiconductor materials that offer both high carrier mobilities and substantial capacitances in electrolytes. In this study, they present ECTs constructed from highly oriented 2D conjugated metal-organic frameworks (2D c-MOFs). The ion-conductive vertical nanopores created within the films of 2D c-MOFs facilitate efficient ion transfer throughout the bulk material, resulting in high volumetric capacitance and enabling the devices to achieve rapid response times and ultrahigh transconductance. Ultraflexible device arrays have been successfully employed for wearable on-skin ECG signal recording in multiple directions, producing a variety of waveforms that are comparable to those obtained from multiload ECG measurement systems for heart condition monitoring. These findings demonstrate that 2D c-MOFs are outstanding semiconductor materials for high-performance ECTs, with promising prospects for applications in flexible and wearable electronics[31]

In this similar study, Conductive MOFs are increasingly recognized as promising electrocatalytic materials due to their unique porous architectures, large pore volumes, numerous catalytically active sites, and high crystallinity. The synthesis of nanorods of the conductive compound Ni_3(2,3,6,7,10,11-hexaiminotriphenylene)$_2$ ($Ni_3(HITP)_2$), achieved from HITP ligands and Ni^{2+} ions, resulting in a high degree of crystallinity. The screen-printed electrodes made from this material were utilized to develop an enzyme-free sensor for detecting ascorbic acid (AA). The sensor exhibited substantial catalytic activity during the electrocatalytic analysis of AA in alkaline conditions, which can be attributed to the synergistic effects of the highly active Ni-N sites. Furthermore, a sensitive and portable enzyme-free detection system for ascorbic acid was designed, leveraging conductive and highly crystalline $Ni_3(HITP)_2$ as the sensing material. This system was integrated with a smartphone using an application-specific integrated circuit equipped with Bluetooth 5.0 capabilities, demonstrating effective electrocatalytic performance for accurately monitoring ascorbic acid levels in sweat.[130]

In this similar study, MOFs have attracted considerable interest in the creation of stretchable and wearable conductive hydrogels for flexible transducers. However, the incorporation of MOFs in hydrogel networks has faced challenges due to their low mechanical performance and poor dispersibility in aqueous solutions, which negatively impact hydrogel properties such as toughness, self-recovery, operational range, conductivity, and response-recovery times. To overcome these limitations, a novel strategy was employed involving micelle co-polymerization for the ex-situ synthesis of Zn-MOF-based hydrogels, resulting in exceptional stretchability, enhanced toughness, anti-fatigue characteristics, and satisfactory conductivity. This innovation incorporated Zn-MOFs into hydrophobically cross-linked polymer chains through an ex-situ method. The micelles of EHDDAB served a dual purpose: they facilitated the uniform dispersion of Zn-MOFs while dynamically cross-linking the polymer chains, significantly enhancing the mechanical properties of the hydrogels. The non-covalent synergistic interactions provided by the Zn-MOFs enabled the hydrogels to achieve high stretchability, substantial stress tolerance, rapid self-recovery, anti-fatigue attributes, and conductivity without requiring external stimuli. Moreover, these Zn-MOF-based hydrogels can function as durable and highly sensitive flexible transducers, capable of detecting various mechanical deformations with rapid response-recovery times and high gauge factors. As a result, they can be customized to act as wearable strain sensors that monitor significant human joint movements, such as wrist bending, as well as finger and elbow motions. Additionally, they are effective in tracking subtle human activities, including speech pronunciation, differentiating between words, and detecting swallowing and laryngeal vibrations during various tasks. Beyond these functionalities, the hydrogels can reliably distinguish and reproduce different written words. The Zn-MOF-based hydrogels show promising potential for applications in electronic skin, medical monitoring, soft robotics, and flexible touch panels.[131]

5.2.2. Applications of MOFs in Implantable Devices

Coatings of MOFs have been identified as having potential applications in surface modification for medical implants, tissue engineering, and drug delivery systems. Therefore, the development of an applicable method for surface-mounted MOF engineering to fabricate protective coatings for implant tissue engineering is recognized as a crucial issue. Additionally, the coating process has been designed for drug infusion while opposing chemical and mechanical resistance. In this similar study, the techniques of MOF coatings for medical applications in both in vitro and in vivo settings are discussed, including in situ growth of MOFs, dip coating of MOFs, spin coating of MOFs, layer-by-layer methods, spray coating of MOFs, gas phase deposition of MOFs, and electrochemical deposition of MOFs. The current study investigates the modification of the implant surface to change the properties of the alloy surface through MOF application to improve characteristics such as the reduction of biofilm adhesion, prevention of infection, enhancement of drug and ion release rates, and corrosion resistance. It is suggested that MOF coatings on the surface of alloys can be considered both an opportunity and a restriction. The presence of MOF coatings in the outer layer of alloys is expected to significantly demonstrate biological, chemical, and mechanical effects. Additionally, the impacts of MOF properties and specific interactions with the surfaces of alloys on antimicrobial resistance, anti-corrosion measures, and the self-healing capabilities of MOF coatings are reported. Thus, the importance of multifunctional methods to improve the adhesion of alloy surfaces, microbial resistance, and corrosion resistance is summarized.[132]

In a similar study, Stretchable and conductive hydrogels are rapidly emerging as candidates for the next generation of wearable devices. However, the limited applications of traditional conductive hydrogels have been attributed to their poor electroactivity and bio adhesiveness. In this study, a mussel-inspired strategy is proposed for the preparation of a specific core–shell redox-active system, consisting of a polydopamine (PDA) modified zeolitic imidazolate framework 71 (ZIF-71) core and a poly 3,4-ethylenedioxythiopene (PEDOT) shell. Owing to the abundance of catechol groups, the assembly of PEDOT on the surface of

ZIF-71 is facilitated, creating a redox-active system. The core–shell nanoparticles are capable of acting as redox-active nanofillers to develop a conductive polyacrylamide (PAM) hydrogel with energy-storage properties. The core–shell PEDOT@PZIF-71 system provides a mussel-inspired environment within the hydrogel matrix, endowing the hydrogel with stretchability and adhesiveness. Hydrogel can be applied as a functional electrode for both bioelectronics and supercapacitors. Moreover, favorable biocompatibility is exhibited by this hydrogel, allowing it to be implanted in vivo for Bio Signal.[132]

Wang et al. strain-induced self-rolled-up nanomembranes are utilized as a device platform for micro-supercapacitors (MSC) in personalized healthcare. Their ultrasmall volume and robust self-protective mechanical properties render them a cutting-edge solution for tiny, intravascular implants and microrobots operating within the human body. Indeed, energy (7.73 μW h cm^{-2}) and power (17.8 mW cm^{-2}) densities are achieved by PEDOT-based tubular MSC, along with 94.1% capacitance retention after 5000 cycles, which performs better than electrolytic capacitors. The incorporation of PEDOT, a well-established biocompatible synthetic polymer, into these systems eliminates the need for toxic or corrosive materials typically used in standard MSCs, ensuring complete biocompatibility for the tubular nano-bio supercapacitor (nBSC). However, it should be noted that adverse reactions caused by this device can still be significantly higher than those caused by natural materials in biological environments.[133]

Advanced wireless sensors, incorporating MOFs, enzymatic systems, and nanocomposites, are offered as unparalleled solutions for monitoring analytes and human physiological signals. When used with external devices, these cutting-edge sensors enable real-time monitoring of analytes and physicochemical processes within the human body, thereby enhancing the understanding of complex biological systems. Ahmadi et al. present advancements in sensor development, fabrication techniques, and user-friendly protocols. The performance of these sensors is evaluated based on their selectivity, sensitivity, and detection limits. Moreover, limitations, challenges, and key strategies to enhance analyte recognition from onsite environmental and biological species are explored, ensuring human point-of-care safety.[134]

MOFs are exhibited as having attractive properties such as highly accessible surface area, large porosity, tunable pore size, and built-in redox-active metal sites. They may serve as excellent candidates for constructing implantable flexible devices for biochemical sensing due to their high thermal and solution stability. However, MOF-based sensors have mostly been reported for in vitro chemical sensing; their use in implantable chemical sensing and in combination with flexible electronics to achieve excellent mechanical compatibility with tissues and organs has rarely been summarized. This study by Li et al. systematically reviews the biochemical sensors based on MOFs and discusses the feasibility of achieving implantable biochemical sensing through MOF-based flexible electronics. The properties of MOFs and underlying mechanisms are introduced, followed by a summarization of different biochemical sensing applications. Strategies to integrate MOFs with flexible devices are supplied from the standpoints of matching mechanics and compatible fabrication processes. Issues that should be addressed in the development of flexible MOF sensors and potential solutions are also provided, followed by perspectives for future applications of flexible MOF sensors. Their work may serve as a reference to offer potential guidelines for the development of flexible MOF-based biochemical sensors that may benefit future applications in personal healthcare, disease diagnosis and treatment, and fundamental studies of various biological processes.[135]

5.3. Environmental Sensors and Energy Management Systems

The development of high-energy storage devices has been propelled by the exploration of new materials in the field of organic supercapacitors. Organic supercapacitors are considered suitable candidates for high-end storage device applications due to their attractive properties, such as high energy density, reduced device weight, excellent cycling stability, and impressive pseudo-capacitive characteristics. Biswas et al. provide an overview of the advancements and future directions of organic supercapacitors. The production and storage of sustainable energy rely on the availability of low-cost, large supercapacitor packs with high energy density. With their high pseudo-capacitance, lightweight form factor, and enhanced device potential, organic supercapacitors present viable alternatives to other energy storage devices. Ongoing research efforts are focused on organic electrolytes and the material aspects of organic supercapacitors. Their work summarizes the current status of research and the underlying chemistry of the storage mechanisms in organic supercapacitors, aiming to address challenges and enhance performance for future applications.[136]

An economically and environmentally sustainable approach to address concerns related to the energy crisis is the recycling of discarded PET (polyethylene terephthalate) plastics into value-added products for the aforementioned applications. In this work by Wang et al., a high surface area Cu-MOF was synthesized through a cost-effective method using waste PET plastic. However, the electrochemical properties of pristine MOFs are limited due to their poor stability and low intrinsic conductivity. Therefore, high-performance nanocomposites of Cu-MOF with conducting polymers, such as PANI (polyaniline) and PPy (polypyrrole), were synthesized via an in situ hydrothermal technique. The incorporation of PANI and PPy not only enhances the conductivity of the nanocomposite but also establishes additional transport channels between MOF and PANI, thereby ensuring effective electrolyte ion transport and improving the overall electrochemical performance. The Cu-MOF/PANI and Cu-MOF/PPy nanocomposites exhibited high specific capacitances of 160.5 and 132.5 F g^{-1}, respectively, at a current density of 0.5 A g^{-1}, surpassing the specific capacitance of pristine Cu-MOF (104.8 F g^{-1}). Furthermore, asymmetric hybrid supercapacitor devices (Cu-MOF//Cu-MOF/PANI and Cu-MOF//Cu-MOF/PPy) were assembled, demonstrating significant potential as energy storage devices. The Cu-MOF//Cu-MOF/PANI hybrid device delivered a high energy density of 51.4 Wh kg^{-1} at a power density of 474 W kg^{-1}, exhibiting outstanding cyclic stability with only a 6.6% reduction in performance after 10000 charge–discharge cycles.[137]

The surge in interest surrounding energy storage solutions, propelled by the demand for electric vehicles and the global energy crisis, has highlighted the effectiveness of carbon-based supercapacitors in fulfilling high-power requirements.

Simultaneously, MOFs have gained recognition as templates for integration with graphene oxide (GO) in composite materials, which have emerged as a promising pathway for developing high-power supercapacitors. This integration elevates the efficiency, cyclic stability, and durability of smart supercapacitors, providing critical insights for addressing contemporary energy storage challenges. The identified combination leverages the strengths of both materials, showcasing substantial potential for advancing energy storage technologies in a sustainable and efficient manner. In this similar study, in which the properties, rationale, and integration of MOF/GO composites have been critically examined. Various fabrication techniques have been thoroughly analyzed, highlighting the specific attributes of MOFs, such as high surface area and modifiable porosity, alongside the conductive and stabilizing characteristics of graphene oxide. Electrochemical characterizations and the physicochemical mechanisms underlying MOF/GO composites have been explored, emphasizing their synergistic interactions that lead to superior electrical conductivity, mechanical robustness, and energy storage capacity. Their research article aims to serve as a concise and insightful resource for researchers engaged in tackling the pressing energy storage issues of our time through the exploration of MOF/GO composites in smart supercapacitors.[96]

The increasing demand for timely and accurate monitoring and control of environmental pollution necessitates the development of new sensing techniques with outstanding performance, characterized by high sensitivity, high selectivity, and reliability. MOFs, also referred to as porous coordination polymers, represent a fascinating class of highly ordered crystalline coordination polymers that are formed through the coordination of metal ions or clusters with organic bridging linkers or ligands. Due to their unique structures and properties—including high surface area, tailorable pore size, high density of active sites, and high catalytic activity—various MOF-based sensing platforms have been reported for the detection of environmental contaminants, such as anions, heavy metal ions, organic compounds, and gases. This study by Fang et al. introduces recent advancements in MOF-based environmental sensors, with a focus on optical, electrochemical, and field-effect transistor sensors. These sensors have demonstrated unique and promising performance in the detection of water and gas contaminants. Furthermore, the incorporation of other functional materials into MOF-based composites has been shown to significantly enhance sensor performance.[138]

The deployment of MOFs in various analytical and bioanalytical applications is recognized as a growing area of research. Their unique properties, including high yet tunable porosity, well-defined channels or pores, and the ease of post-synthetic modification to incorporate additional functional units, render them ideal candidates for sensing applications. This potential arises from the interaction between analytes and a MOF, which often results in structural changes that lead to modifications in the intrinsic physicochemical properties of the MOF, subsequently transduced into measurable signals. The high porosity facilitates efficient adsorption of analytes, while the tunable nature of pore sizes and the installation of specific recognition groups allow modulation of the affinity toward various classes of compounds, contributing to enhanced sensor sensitivity and selectivity, respectively. Illustrative figures are provided to demonstrate the potential of MOF-based sensors in the most relevant application fields, and future challenges and opportunities for their translation from academia (i.e., laboratory testing of MOF sensing properties) to industry (i.e., real-world analytical sensor devices) are critically discussed.[139]

Over the last decade, the usage of MOFs for electrochemical applications has gained popularity. One of the most commonly encountered electrochemical sensing systems is the amperometry sensor, which utilizes sensitivity as the sensing response for the targeted analyte. Electrocatalysts exhibiting high reaction rates and the capability to selectively react with the intended analyte are generally required. As electrochemical reactions occur only on the surface of an electrode, a typical technique for constructing the active electrode of an amperometry sensor involves the deposition or immobilization of the electrocatalyst on the electrode surface to produce a modified electrode. It is known that multiple chemical functionalities can be incorporated into the entire pore structure of MOFs through various synthetic routes while maintaining significant porosity. However, the chemical stability of most MOFs in water poses a major challenge, as most electrochemical sensing systems require the use of aqueous electrolytes. Recently, significant efforts have been made to manufacture MOFs using biomimetic mineralization methods, wherein biomolecules serve as crystallization and guiding agents for the design of various MOFs. MOF-based particles containing biomolecules such as enzymes, proteins, peptides, cells, DNA, and viruses have been synthesized using this approach. Miri et al. summarize recent developments in MOF-biomolecule composites, with special emphasis placed on preparative techniques and the synergistic effects of biomolecules and MOFs. Applications of MOF-biomolecule composites in electro-sensing are also presented.[140]

The production of synthetic drugs is regarded as a significant milestone in the healthcare sector, leading to transformations in the overall health, aging, and lifestyle of the general population. Due to the surge in production and consumption, pharmaceutical drugs have been identified as potential environmental pollutants that are toxic and exhibit low biodegradability. Traditional chromatographic techniques currently in use are recognized for being time-consuming and expensive, despite offering good precision. Alternatively, electroanalytical techniques have recently been identified as selective, rapid, sensitive, and more straightforward for drug detection. MOFs are acknowledged for their intrinsic porous nature, high surface area, and diversity in structural design, which provide credible drug-sensing capabilities. Long-term reusability and the maintenance of chemo-structural integrity present major challenges that are addressed through ligand–metal combinations, optimization of synthetic conditions, functionalization, and direct growth of MOFs over the electrode surface. Moreover, chemical instability and lower conductivities have limited the mass commercialization of MOF-based materials in the fields of biosensing, imaging, drug release, therapeutics, and clinical diagnostics. Rizwan et al. are dedicated to analyzing various combinations of MOFs utilized for the electrochemical detection of pharmaceutical drugs, including antibiotics, analgesics, anticancer agents, antituberculosis medications, and veterinary drugs. Furthermore, the relationship between the composition, morphology, and structural properties of MOFs and their detection capabilities for each drug species is elucidated.[141]

Flexible and portable power sources are essential components of wearable electronic devices. Fabric-based triboelectric nanogenerators (TENGs) have emerged as promising energy sources for wearable electronic devices, as they can generate electrical energy from biomechanical movements with significant flexibility. Jayababu et al. a highly flexible Co/Zn bimetal organic framework-based TENG (BMOF TENG) was fabricated. Co/Zn BMOF nanosheets were easily prepared and coated on flexible conductive fabric (BMOF/FCF), serving as the tribo-positive material against a PTFE/Al-based tribo-negative material for the construction of the BMOF TENG. The content of Zn was varied from 0% to 50% to optimize the electrical output, revealing that 15% Zn content was appropriate for achieving superior electrical output. The open circuit voltage, short circuit current, and charge density of the BMOF TENG increased from 11 V to 47 V, from 1.06 μA to 7 μA, and from 4 nC cm^{-2} to ≈17 nC cm^{-2}, respectively, as the Zn content increased from 0% to 15%. Thus, the optimized Zn content in Co/Zn BMOF contributed to an enhancement of the electrical output of the BMOF TENG by nearly 450%. The output power of the BMOF TENG was found to be 1.1 mW m^{-2} at a load resistance of 2 MΩ. Given that the phenomenon of gas sensing is largely associated with the material's surface, the unique surface features of the BMOF/FCF were utilized for sensing hazardous gases. Variations in electrical output were observed in the presence of air and targeted gases, demonstrating good selectivity toward ammonia at room temperature. Ultimately, the BMOF TENG proposed in this study is capable of converting mechanical energy into electrical energy and can be employed as an ammonia sensor in environmental monitoring and food quality assessment (Figure 3F).[142]

The issue of environmental pollution is recognized as one of the most significant challenges in the modern world. Pollution has been linked to an increase in human diseases, the extinction of numerous species of plants and animals, global warming, and various weather anomalies. A major challenge for scientists is the development of methods for monitoring and removing emerging pollutants. This review examines MOFs and their application as materials for constructing different types of sensors for environmental pollution monitoring. Specifically, the detection of heavy metals such as mercury, lead, and arsenic, as well as organic compounds including drugs, biomolecules, and pesticides, is considered. The data collected indicate that photoelectrochemical (PEC) sensors based on MOFs are particularly intriguing due to their diverse combinations (e.g., surface modification) and operational capabilities. PEC sensors demonstrate remarkable sensitivity, which can reach the pica level, positioning them as one of the most effective tools in sensing applications. Yan et al. also address the primary challenges associated with sensors, which primarily relate to the possibilities for sensor reuse, regeneration, and safe disposal. Furthermore, greater emphasis should be placed on the sensor manufacturing process, which often involves toxic compounds, along with research aimed at eliminating these in favor of non-toxic alternatives.[143]

A nano matrix has been prepared containing molybdate (MoO_3) anchored on a zeolitic imidazolate framework (ZIF-8) that supports a CoNi MOF. The synthesized nanocomposite possesses a high surface area of 333.66 m^2 g^{-1} and consists of a mixture of meso- and microporous structures. When the nanostructure is employed as an electrode material, the highest specific capacitance of 1260 F g^{-1} is achieved for the optimal ratio of the MOF. The superior nanocomposite is deposited on carbon cloth and further evaluated as an electrode in a coin-cell-based ($C_2N_1MZ||NGT$) hybrid supercapacitor device, which demonstrates a capacitance of 363 F g^{-1}. Additionally, the nanocomposite is utilized as a transducer in the electrochemical sensing of theophylline (TP). Square-wave voltammetry reveals that the nano matrix exhibits significant electrocatalytic activity and provides a stable redox peak for varying concentrations of TP ranging from 1 μM to 5 M. The limit of detection for the electrochemical sensor is calculated to be 75.4 nM, indicating the sensor's practicality. Therefore, the results obtained suggest that the prepared nanocomposite is suitable for energy storage and sensing applications.[144]

6. Future Potential and Research Directions

Despite the promising potential of MOF-based bioelectronic supercapacitors, several challenges must be addressed to realize their full capabilities. These challenges include issues related to the stability of MOFs under operational conditions, which may lead to degradation and loss of performance over time. Additionally, the complexity of the synthesis and functionalization processes can result in inconsistencies in material properties, making it difficult to achieve reproducible results. The integration of biological components with electronic systems also presents hurdles, such as biocompatibility and the need for effective interface management between biological and electronic materials. Furthermore, the scaling up of production techniques for commercial applications remains a significant barrier, necessitating further research into cost-effective and scalable synthesis methods.

MOFs are promising materials known for their high surface area and customizable structures. However, there are several potential challenges that could hinder their performance. One key issue is their naturally low electrical conductivity, which may result in reduced performance, particularly in applications like supercapacitors that require high power density.[18] Additionally, the biocompatibility of MOFs can vary depending on the specific metal ions and organic ligands used; some MOFs may be toxic or incompatible with biological systems.[145] Another limitation is their susceptibility to environmental factors such as humidity, pH fluctuations, and high temperatures, which can lead to structural degradation and performance loss over time. The synthesis of MOFs is also complex and time-consuming, contributing to higher production costs.[146]

Moreover, some MOFs may offer lower energy density compared to other materials used in energy storage applications. To overcome these challenges, it is crucial to improve their conductivity, ensure their biocompatibility, enhance their stability, and streamline their synthesis processes.

Future research should focus on the development of next-generation MOF-based materials that enhance the performance of bioelectronic supercapacitors. This could involve the design of MOFs with tailored properties, such as increased surface area, enhanced conductivity, and improved chemical stability. The exploration of new metal and organic linkers may also lead to innovative structures with superior performance characteristics. Furthermore, combining MOFs with other nanomaterials, such as carbon-based materials or conductive polymers, may provide synergistic effects that enhance overall functionality. The incorporation of smart materials that can respond to environmental stimuli could also expand the applications of MOF-based bioelectronic supercapacitors, making them more versatile in various biomedical and energy storage contexts.

MOFs have become ideal candidates for energy storage systems, fueled by the growing interest in the use of dynamically responsive materials. MOFs are of great interest due to their ability to adjust their electronic behavior when exposed to external influences. Thanks to this property, they are considered ideal candidates for renewable energy technologies, especially energy storage systems such as bioelectronic supercapacitors. Such energy storage devices enable efficient energy storage and fast charge/discharge cycles by using materials that can adapt to environmental changes. In particular, the use of photochromic molecules has proven to be effective in triggering dynamic behaviors. The incorporation of these molecules into different hybrid matrices makes it possible to tune the structures and connectivity of the materials. These developments enable materials to have better-controlled properties and to respond to external triggers and optimize their performance. In the context of bioelectronic supercapacitors, these improvements in material characteristics are particularly important. The ability of MOFs to dynamically adjust their electronic and ionic conductivity in response to stimuli such as light or pressure could result in supercapacitors with higher energy density, faster charging times, and improved long-term stability. These dynamic materials hold significant promise for advancing energy storage and conversion, positioning them as a leading candidate for next-generation energy devices.[147]

MOFs have attracted attention as promising materials for bioelectronic supercapacitors thanks to their nanosim activities. Their high surface area, tunable porosity, and biocompatibility make them ideal candidates for use as biomimetic catalysts and electrocatalytic interfaces. In particular, MOFs incorporating metalloporphyrins exhibit enzyme-like behavior, facilitating key reactions such as hydrogen peroxide reduction and oxygen reduction. These characteristics contribute significantly to enhancing the efficiency and functionality of bioelectronic supercapacitors.[148]

The advancement of integration techniques is crucial for the development of multifunctional devices that combine energy storage with biological sensing capabilities. Research should focus on innovative strategies for integrating MOF-based supercapacitors with biosensors to create compact, efficient, and effective devices. Techniques such as layer-by-layer assembly, 3D printing, and microfabrication should be explored to facilitate the seamless integration of different functionalities into a single device. Additionally, developing self-powered systems that utilize the energy generated from biological processes to power biosensors and other electronic components could pave the way for groundbreaking applications in health monitoring and environmental sensing. Exploring these integration techniques will enhance the practicality and usability of MOF-based bioelectronic supercapacitors in real-world applications.

Metal-organic frameworks have gained increasing attention due to their high porosity, tunable properties, and versatile applications in biomedical and energy storage systems. Their potential in bioelectronic applications, particularly as biosensors and supercapacitors, has been extensively explored. However, while many studies provide valuable insights into MOF-based biosensors, discussions on future directions and novel design strategies remain limited. This work aims to address this gap by integrating findings from existing research while emphasizing the need for further innovation in MOF-based bioelectronic supercapacitors.

Glucose oxidase (GOx, EC 1.1.3.4) is a widely studied enzyme due to its role in catalyzing the oxidation of glucose to gluconic acid. Its integration into MOF structures, such as zeolitic imidazolate framework-8 (ZIF-8), has led to significant improvements in enzyme stability, catalytic efficiency, and tolerance to environmental factors. These GOx-MOF hybrids demonstrate exceptional sensitivity in glucose detection, with detection limits as low as 0.5 μM, making them suitable for clinical applications. Despite these advances, there is still a need to develop MOF composites with enhanced biocompatibility and real-time monitoring capabilities to facilitate their transition from laboratory research to practical biomedical applications.

Dopamine, a crucial neurotransmitter, plays a vital role in neurological functions and is a key biomarker for disorders such as Parkinson's disease and schizophrenia. Traditional electrochemical sensors face challenges related to thermal stability and long-term accuracy. To overcome these limitations, researchers have developed phase-change material (PCM)-based electroactive microcapsules with MOF-anchored polypyrrole/SiO_2 double-layered shells. These structures enable effective thermal regulation, maintaining enzymatic bioactivity at elevated temperatures. Experimental results indicate that these biosensors offer a high sensitivity of $3.541\ \mu A \cdot L \cdot \mu mol^{-2} \cdot cm^{-1}$ and a detection limit as low as $0.0069\ \mu mol \cdot L^{-1}$ at 50 °C. Such advancements highlight the potential of MOF-based biosensors in high-temperature biomedical applications, yet further research is needed to ensure their durability and integration into wearable bioelectronic devices.[149]

Melatonin (MEL) is a sleep-regulating hormone whose abnormal levels are linked to disorders such as hypertension, stress, and Alzheimer's disease. A novel sensing platform combining Nb_2CT_x MXene nanosheets with a zinc-based MOFhas demonstrated remarkable electrocatalytic properties and improved electrical conductivity. The synergistic effect of MOF nanoflakes and MXene nanosheets significantly enhances electrochemical performance for MEL detection, yielding a wide linear range of 1–100 μM and a detection limit of 215 nM. Furthermore, practical tests in biological fluids, including sweat, blood serum, and cerebrospinal fluid, have validated the sensor's applicability in real-time medical diagnostics. The potential integration of such biosensors into wearable health monitoring devices represents a promising future direction for MOF-based bioelectronics.[150]

Hydrogen peroxide (H_2O_2) is a crucial metabolic byproduct, and its detection is essential in both physiological and pathological studies. The immobilization of catalase (CAT) within MOFs has enabled efficient electrochemical sensing of H_2O_2 with high stability and reproducibility. Similarly, MOF-based biosensors have been instrumental in detecting cancer biomarkers such as protein tyrosine kinase-7 (PTK7), lymphocyte activating gene-3 (LAG-3), and prostate-specific antigen (PSA). These biosensors utilize techniques such as fluorescence, mass spectrometry, and electrochemistry for precise tumor detection. Future studies should focus on integrating these biosensors with advanced imaging techniques, such as confocal microscopy, to improve in vivo tumor monitoring and early-stage cancer diagnostics.[151]

Beyond biosensing, MOFs have shown immense potential in energy storage applications, particularly in bioelectronic supercapacitors. Their high surface area and tunable pore structures allow for efficient ion transport and enhanced charge storage. Recent studies have demonstrated that enzyme-MOF hybrids can function as bioelectronic supercapacitors, enabling sustainable energy harvesting in implantable medical devices. The incorporation of conductive polymers, such as polyaniline and polypyrrole, further enhances charge transfer efficiency. However, key challenges, including stability under physiological conditions and long-term biocompatibility, must be addressed to advance these systems toward real-world biomedical applications.

A promising approach in the development of MOF-based bioelectronic supercapacitors and biosensors involves the integration of conductive polymers such as polypyrrole (PPy) with MOFs. Recent studies have fabricated conductive nanocomposites of copper metal-organic frameworks and PPy to exploit the electrical conductivity of PPy and the porosity of MOFs. These PPy/Cu-MOF nanocomposites have demonstrated superior capacitance and electrochemical properties compared to pure materials, making them ideal candidates for biosensing and energy storage applications.[152]

Additionally, in vitro studies on 3T3 fibroblasts, MCF-7 breast cancer cells, and J774.A1 macrophages have shown that these nanocomposites exhibit excellent biocompatibility with minimal cytotoxicity. Hemolysis assays confirmed low hematological toxicity, while in vivo tests in mice revealed no significant inflammatory responses or liver toxicity post-injection. These findings suggest that PPy/Cu-MOF nanocomposites hold great potential for next-generation biomedical applications, including biosensors and controlled drug delivery systems. Future research should focus on enhancing the long-term stability and functionalization of these composites for seamless integration into wearable and implantable medical devices.[152]

Another emerging approach in MOF-based biosensing involves the combination of Cu-MOF with graphene oxide (GO) to enhance electrocatalysis, stability, and conductivity. A recent study introduced a GO/Cu-MOF nanocomposite for the simultaneous electrochemical detection of two biomarkers associated with lower respiratory infections: Mycoplasma pneumoniae (M. pneumoniae) and Legionella pneumophila (L. pneumophila). The immunosensor was developed by modifying screen-printed electrodes with the GO/Cu-MOF composite and functionalizing them with monoclonal antibodies for specific antigen detection. The platform demonstrated excellent sensitivity over a broad concentration range, making it a promising candidate for environmental pathogen monitoring. The synergistic interactions between GO and MOF contributed to the enhanced electrochemical performance, highlighting the potential of MOF-based immunosensors for rapid, on-field diagnostic applications.[74]

While MOF-based bioelectronic supercapacitors and biosensors hold immense promise for biomedical and energy applications, existing research primarily focuses on fundamental studies rather than practical implementation. Future efforts should prioritize the development of MOF composites with improved biocompatibility, real-time monitoring capabilities, and seamless integration with wearable and implantable devices. By addressing these challenges, MOF-based technologies can significantly contribute to advancements in personalized medicine, diagnostic tools, and sustainable bioelectronics.

Future research on MOF-based supercapacitors should focus on designing novel MOF structures and developing composite strategies to enhance electrical performance and multifunctionality. One promising approach is the integration of conductive materials such as graphene, MXenes, or carbon nanotubes to improve charge transport while maintaining the intrinsic porosity of MOFs. Additionally, tuning MOF structures through rational ligand design, redox-active linkers, and metal node modifications can enhance charge mobility and electrochemical performance. Beyond conductivity improvements, the development of multifunctional MOFs with electrocatalytic or battery-like properties could enable hybrid energy storage and conversion devices. Moreover, addressing the long-term stability and scalability of MOF-based supercapacitors through robust framework engineering and cost-effective synthesis methods is crucial for practical applications. By pursuing these strategies, MOF-based supercapacitors can overcome current limitations and evolve into high-performance, next-generation energy storage solutions.

7. Conclusions and Future Perspectives

The research conducted on MOF-based bioelectronic supercapacitors highlights their potential as innovative solutions for energy storage in biomedical applications. The unique structural and functional properties of MOFs contribute significantly to the performance of these devices, making them suitable for integration with biological systems. Key findings indicate that optimizing the synthesis and functionalization processes, as well as enhancing the interaction between biological and electronic components, are critical for advancing the field. Additionally, the exploration of diverse applications in health technologies, wearable devices, and environmental sensors demonstrates the versatility and applicability of MOF-based bioelectronic supercapacitors.

Looking ahead, the potential applications of MOF-based bioelectronic supercapacitors are vast and varied. Their incorporation into wearable health monitoring devices, implantable biosensors, and environmental monitoring systems can revolutionize how data is collected and utilized in real-time. Innovreal timeations in MOF materials and integration techniques will drive the development of more sophisticated devices that can operate autonomously, providing crucial insights into health and environmental conditions. The exploration of novel functionalities, such as self-sustaining energy sources and advanced sensing capabilities, will further enhance their utility in various sectors.

The commercial and industrial potential of MOF-based bioelectronic supercapacitors is significant, given the growing demand for efficient and sustainable energy storage solutions in biomedical and environmental applications. As research continues to address existing challenges, the pathway to commercialization will become clearer. Collaborations between academia and industry can facilitate the translation of research findings into market-ready products, driving innovation and economic growth. The successful commercialization of these technologies may also contribute to the development of smart healthcare solutions and sustainable energy systems, underscoring the importance of continued investment in this promising field.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

bioelectronics, electrical, MOFs, tissue engineering, wearable material

Received: December 31, 2024
Revised: February 16, 2025
Published online:

[1] C. N. Hong, A. B. Crom, J. I. Feldblyum, M. R. Lukatskaya, *Chem.* **2023**, *7*, 798.
[2] V. F. Yusuf, N. I. Malek, S. K. Kailasa, *ACS Omega.* **2022**, *7*, 44507.
[3] K. O. Otun, A. Mukhtar, S. A. Nafiu, I. T. Bello, J. Abdulsalam, *J. Energy Storage* **2024**, *84*, 110673.
[4] G. Ganesh, *Int. J. Res. Pub. Rev.* **2022**, *4*, 2074.
[5] H. Meskher, S. B. Belhaouari, F. Sharifianjazi, *Heliyon* **2023**, *9*, e21621.
[6] A. E. Baumann, D. A. Burns, B. Liu, V. S. Thoi, *Commun. Chem.* **2019**, *2*, 86.
[7] R. Du, Y. Wu, Y. Yang, T. Zhai, T. Zhou, Q. Shang, L. Zhu, C. Shang, Z. Guo, *Adv. Energy Mater.* **2021**, *11*, 2100154.
[8] S. Wang, et al., *Angew. Chem. – Int. Ed.* **2015**, *54*, 14738.
[9] X. Wang, J. Niu, M. K. Hadi, Q. Zhou, D. Wang, F. Ran, *J. Energy Storage* **2024**, *99*, 113263.
[10] C. Sen Liu, et al., *Biosens. Bioelectron.* **2017**, *91*, 804.
[11] D. Gan, Z. Huang, X. Wang, D. Xu, S. Rao, K. Wang, F. Ren, L. Jiang, C. Xie, X. Lu, *Mater. Horiz.* **2023**, *10*, 2169.
[12] A. M. Al-Enizi, A. Nafady, N. B. Alanazi, M. M. Abdulhameed, S. F. Shaikh, *Chemosphere* **2024**, *350*, 141080.
[13] J. Aguila-Rosas, D. Ramos, C. T. Quirino-Barreda, J. A. Flores-Aguilar, J. L. Obeso, A. Guzmán-Vargas, I. A. Ibarra, E. Lima, *Chem. Commun.* **2023**, *59*, 11753.
[14] A. N. Yang, J. T. Lin, C. T. Li, *ACS Appl. Mater. Interf.* **2021**, *13*, 8435.
[15] J. G. Park, M. L. Aubrey, J. Oktawiec, K. Chakarawet, L. E. Darago, F. Grandjean, G. J. Long, J. R. Long, *J. Am. Chem. Soc.* **2018**, *140*, 8526.
[16] N. Kitchamsetti, D. Kim, *J. Alloys Compd.* **2023**, *959*, 170483.
[17] B. Shao, H. Chen, C. Cui, J. Li, R. Gonge, *Chem. Lett.* **2021**, *50*, 714.
[18] R. Saha, K. Gupta, C. J. Gómez García, *Cryst. Growth Des.* **2024**, *24*, 2235.
[19] A. Afruz, M. Amiri, M. Kaffash-Jamshid, A. Bezaatpour, P. Bottke, M. Wark, *Electrochim. Acta* **2025**, *513*, 145586.
[20] B. R. Paul Nagarajan, D. Dhinasekaran, B. Subramanian, A. R. Rajendran, *ACS Appl. Nano Mater.* **2024**, *7*, 23999.
[21] K. Kuruvinashetti, J. Li, Y. Zhang, H. Bemana, M. McKee, N. Kornienko, *Chem. Phys. Rev.* **2022**, *3*, 021306.
[22] H. R. Abid, M. R. Azhar, S. Iglauer, Z. H. Rada, A. Al-Yaseri, A. Keshavarz, *Heliyon.* **2024**, *10*, e23840.
[23] Z. Di, Y. Qi, X. Yu, F. Hu, *Catalysts.* **2022**, *12*, 1582.
[24] D. Kim, M. Kang, H. Ha, C. S. Hong, M. Kim, *Coord. Chem. Rev.* **2021**, *438*, 213892.
[25] X. Zhang, S. Zhang, Y. Tang, X. Huang, H. Pang, *Composites, Part B* **2022**, *230*, 109532.
[26] J.-W. Yu, H.-J. Yu, Z.-Y. Yao, Z.i-H. Li, Q. Ren, H.-B. Luo, Y. Zou, L. Wang, X.-M. Ren, *Cryst. Eng. Comm.* **2021**, *23*, 6093.
[27] A. Benny, S. D. Kalathiparambil Rajendra Pai, D. Pinheiro, S. J. Chundattu, *Res. Chem.* **2024**, *7*, 101414.
[28] L. Sun, C. H. Hendon, S. S. Park, Y. Tulchinsky, R. Wan, F. Wang, A. Walsh, M. Dinca, *Chem. Sci.* **2017**, *8*, 4450.
[29] H. Li, et al., *ACS Appl. Mater. Interf.* **2018**, *10*, 3160.
[30] T. Xu, Y. Wang, Y. Xue, J. Li, Y. Wang, *Chem. Eng. J.* **2023**, *470*, 144247.
[31] J. Song, et al., *Sci. Adv.* **2023**, *9*.
[32] X. Dao, M. Nie, H. Sun, W. Dong, Z. Xue, Q. Li, J. Liao, X. Wang, X. Zhao, D. Yang, L. Teng, *Int. J. Hydrogen Energy* **2022**, *47*, 16741.
[33] M. Z. Iqbal, M. M. Faisal, S. R. Ali, S. Farid, A. M. Afzal, *Electrochim. Acta* **2020**, *346*, 136039.
[34] Z. Chen, Y. Cui, C. Ye, L. Liu, X. Wu, Y. Sun, W. Xu, D. Zhu, *Chem. – A Eur. J.* **2020**, *26*, 12868.
[35] H. Rong, P. Song, G. Gao, Q. Jiang, X. Chen, L. Su, W.-L. Liu, Q.i Liu, *Dalton Trans.* **2023**, *52*, 1962.
[36] J. Wang, Q. Zhong, Y. Xiong, D. Cheng, Y. Zeng, Y. Bu, *Appl. Surf. Sci.* **2019**, *483*, 1158.
[37] S. G. Priya, in *Biosensors: Developments, Challenges and Perspectives*, (Eds. R. Mathew, and J. Ajayan), Singapore: Springer Nature, Singapore, **2024**, pp. 1–12.
[38] J. Wu, H. Liu, W. Chen, B. Ma, H. Ju, *Nat. Rev. Bioeng.* **2023**, *1*, 346.
[39] C. Chen, J. Wang, *Analyst* **2020**, *145*, 1605.
[40] M. Wang, J. Huang, Q.-A. Huang, *Microsyst. Nanoeng.* **2024**, *10*, 202.
[41] V. S. Sukanya, S. N. Rath, *Adv. Exp. Med. Biol.* **2022**, *1379*, 319.
[42] H. Singh Jhinjer, M. Jassal, A. K. Agrawal, *Chem. Eng. J.* **2023**, *478*, 147253.
[43] R. Sakthivel, L.u-Y. Lin, Y.-F. Duann, H.-H. Chen, C. Su, X. Liu, J.r-H. He, R.-J. Chung, *ACS Appl. Mater. Interf.* **2022**, *14*, 28639.
[44] A. Mohanty, D. P. Jaihindh, Y. P. Fu, S. P. Senanayak, L. S. Mende, A. Ramadoss, *J. Power Sources* **2021**, *488*, 229444.
[45] Y. Huang, J. Wang, X. Ju, S. Zhang, X. Sun, *J. Energy Storage* **2023**, *72*, 108460.
[46] G. Nagaraju, S. C. Sekhar, B. Ramulu, S. K. Hussain, D. Narsimulu, J. S. Yu, *Nano-Micro Lett.* **2021**, *13*, 17.
[47] M. Shaheen, M. Z. Iqbal, M. W. Khan, S. Siddique, S. Aftab, S. M. Wabaidur, *Energy Fuels* **2023**, *37*, 4000.
[48] R. Srinivasan, E. Elaiyappillai, E. J. Nixon, I. Sharmila Lydia, P. M. Johnson, *Inorg. Chim. Acta* **2020**, *502*, 119393.
[49] Y. Cheng, Y. Zhang, H. Jiang, X. Dong, J. Zheng, C. Meng, *J. Colloid Interface Sci.* **2020**, *561*, 762.
[50] Z. Karimzadeh, B. Shokri, A. Morsali, *Appl. Phys. Lett.* **2023**, *123*, 103903.
[51] H. Du, et al., *Chem. Eng. J.* **2022**, *428*, 131994.
[52] Q. Zhang, S. Yan, X. Yan, Y. Lv, *Sci. Total Environ.* **2023**, *902*, 165944.
[53] M. Safaei, M. M. Foroughi, N. Ebrahimpoor, S. Jahani, A. Omidi, M. Khatami, *TrAC – Trends Anal. Chem.* **2019**, *118*, 401.
[54] W. Chai, X. Chen, J. Liu, L. Zhang, C. Liu, L.i Li, J. R. Honiball, H. Pan, X.u Cui, D. Wang, *Regener. Biomater.* **2024**, *902*, 165944.
[55] J. Annamalai, P. Murugan, D. Ganapathy, D. Nallaswamy, R. Atchudan, S. Arya, A. Khosla, S. Barathi, A. K. Sundramoorthy, *Chemosphere* **2022**, *298*, 134184.
[56] A. Asghar, W. A. Ghaly, M. Y. Awaji, O. Hakami, W. M. Alamier, S. K. Ali, M. Y. A. Almashnowi, E. A. Al-Harthi, M. S. Rashid, M. Imran, *J. Electrochem. Soc.* **2024**, *171*, 030526.
[57] D. Y. Lee, S. J. Yoon, N. K. Shrestha, S. H. Lee, H. Ahn, S. H. Han, *Microporous Mesoporous Mater.* **2012**, *153*, 163.
[58] J. Hong, S. J. Park, S. Kim, *Electrochim. Acta* **2019**, *311*, 62.
[59] M. Z. Iqbal, M. Shaheen, A. Khizar, S. Aftab, Z. Ahmad, A. M. Tawfeek, S. Sharif, *RSC Adv.* **2023**, *13*, 22936.
[60] M. Ojha, B. Wu, M. Deepa, *ACS Appl. Mater. Interf.* **2020**, *12*, 42749.
[61] Y. Yang, J. Zhang, W. Liang, J. Zhang, X. Xu, Y. Zhang, R. Yuan, D. Xiao, *Sens. Actuators, B* **2022**, *362*, 131802.
[62] S. Ebrahimi-Koodehi, F. E. Ghodsi, J. Mazloom, *Sci. Rep.* **2023**, *13*, 19260.
[63] I. Hussain, S. Iqbal, C. Lamiel, A. Alfantazi, K. Zhang, *J. Mater. Chem. A* **2022**, 4475.
[64] B. He, Q. Zhang, Z. Pan, L. Li, C. Li, Y. Ling, Z. Wang, M. Chen, Z. Wang, Y. Yao, Q. Li, L. Sun, J. Wang, L. Wei, *Chem. Rev.* **2022**, *10*, 10087.

[65] K. B. Deore, V. N. Narwade, S. S. Patil, S. R. Rondiya, K. A. Bogle, M.-L. Tsai, T. Hianik, M. D. Shirsat, *J. Alloys Compd.* **2023**, *358*, 170412.
[66] W. Shen, X. Guo, H. Pang, *Molecules* **2022**, *27*, 8226.
[67] Y. Hao, H. Guo, F. Yang, J. Zhang, N. Wu, M. Wang, C. Li, W.u Yang, *J. Alloys Compd.* **2022**, *911*, 164726.
[68] T. J. Theka, B. R. J. Thamaga, Z. P. Tshabalala, R. G. Motsoeneng, H. C. Swart, D. E. Motaung, *Appl. Surf. Sci.* **2024**, *644*, 158789.
[69] I. Hussain, S. Iqbal, T. Hussain, W. L. Cheung, S. A. Khan, J. Zhou, M. Ahmad, S. A. Khan, C. Lamiel, M. Imran, A. AlFantazi, K. Zhang, *Mater. Today Phys.* **2022**, *23*, 100655.
[70] M. Z. Iqbal, M. Shaheen, M. W. Khan, S. Siddique, S. Aftab, S. M. Wabaidur, M. J. Iqbal, *RSC Adv.* **2023**, *13*, 2860.
[71] R. Batool, S. D. Dhas, A. C. Mendhe, A. Ghazal, I. Kim, D. Kim, *J. Mater. Chem. A* **2024**, *12*, 21230.
[72] C. Young, J. Kim, Y. V. Kaneti, Y. Yamauchi, *ACS Appl. Energy Mater.* **2018**, *1*, 5.
[73] Shubhangi, I. N., S. K. Rai, P. Chandra, *Talanta* **2024**, *266*, 125124.
[74] A. Ghosh, S. Fathima Thanutty Kallungal, S. Ramaprabhu, *Biosensors* **2023**, *13*, 123.
[75] J. Cao, J. Yun, N. Zhang, Y. Wei, H. Yang, Z. Xu, *Synth. Met.* **2021**, *282*, 116931.
[76] T. Deng, X. Shi, W. Zhang, Z. Wang, W. Zheng, *iScience* **2020**, *23*, 101220.
[77] Z. X. Li, B. L. Yang, K. Y. Zou, L. Kong, M. L. Yue, H. H. Duan, *Carbon* **2019**, *140*, 540.
[78] K. Wang, Z. Wang, J. Liu, C. Li, F. Mao, H. Wu, *ACS Appl Mater. Interf* **2020**, *12*, 47482.
[79] J. Yang, C. Zheng, P. Xiong, Y. Li, M. Wei, *J. Mater. Chem. A* **2014**, *2*, 19005.
[80] S. Sundriyal, H. Kaur, S. K. Bhardwaj, S. Mishra, K. H. Kim, A. Deep, *Coord. Chem. Rev.* **2018**, *369*, 15.
[81] A. Y. Lo, C. C. Chang, Y. W. Lai, P. R. Chen, B. C. Xu, *ACS Omega* **2020**, *5*, 11522.
[82] J. Pokharel, A. Gurung, A. Baniya, W. He, K.e Chen, R. Pathak, B. S. Lamsal, N. Ghimire, Y. Zhou, *Electrochim. Acta* **2021**, *394*, 139058.
[83] R. R. Salunkhe, Y. V. Kaneti, J. Kim, J. H. Kim, Y. Yamauchi, *Acc. Chem. Res.* **2016**, *49*, 2796.
[84] W. Kukulka, K. Cendrowski, E. Mijowska, *Electrochim. Acta* **2019**, *307*, 582.
[85] Y. Wang, X. Zhu, D. Liu, H. Tang, G. Luo, K. Tu, Z. Xie, J. Lei, J. Li, X.i Li, D. Qu, *J. Appl. Electrochem.* **2019**, *49*, 1103.
[86] F. Wang, J. Hu, Y. Peng, X. Wu, H. Xue, H. Pang, *Adv. Sens. Energy Mater.* **2023**, *2*, 100053.
[87] D. Li, A. Yadav, H. Zhou, K. Roy, P. Thanasekaran, C. Lee, *Global Challenges.* **2024**,*8*, 2300244.
[88] M. Yuan, L. Wang, K. Li, Q. Zhang, Y. Li, C. Hou, H. Wang, *Electroanalysis* **2023**, *35*, 202200556.
[89] Y. Xia, T. Su, Z. Mi, Z. Feng, Y. Hong, X. Hu, Y. Shu, *Anal. Chim. Acta* **2023**, *1278*, 341754.
[90] P. N. Blessy Rebecca, D. Durgalakshmi, S. Balakumar, R. A. Rakkesh, *Chem. Eng. J.* **2024**, *484*, 149789.
[91] Y. Shi, Y. Zou, M. Khan, M. Zhang, J. Yan, X. Zheng, W. Wang, Z. Xie, *J. Mater. Chem. C* **2023**, *11*, 3692.
[92] X. Zhu, S. Yuan, Y. Ju, J. Yang, C. Zhao, H. Liu, *Anal. Chem.* **2019**, *91*, 10764.
[93] P. N. Blessy Rebecca, D. Durgalakshmi, S. Balakumar, R. A. Rakkesh, *Sens. Diagn.* **2023**, *2*, 1360.
[94] M. Liu, J. Mou, X. Xu, F. Zhang, J. Xia, Z. Wang, *Talanta* **2020**, *220*, 121374.
[95] C. Wang, Y. Zhang, Y. Liu, X. Zeng, C. Jin, D. Huo, J. Hou, C. Hou, *Anal. Chim. Acta* **2024**, *1299*, 342441.
[96] M. Pooresmaeil, E. A. Asl, H. Namazi, *J. Alloys Compd.* **2021**, *885*, 160992.
[97] J. Liu, X. Zha, Y. Yang, *J. Electrochem. Sci. Technol.* **2024**, *15*, 32.
[98] Y. Haldorai, S. R. Choe, Y. S. Huh, Y. K. Han, *Carbon* **2018**, *127*, 366.
[99] P. Arul, S. A. John, *Electrochim. Acta* **2019**, *306*, 254.
[100] Z. Li, W. Zeng, Y. Li, *Molecules* **2023**, *28*, 4891.
[101] S. A. Zaidi, J. H. Shin, *Talanta* **2016**, *149*, 30.
[102] L. Wang, C. Hou, H. Yu, Q. Zhang, Y. Li, H. Wang, *Chem. Electro. Chem.* **2020**, *7*, 4446.
[103] J. Ding, et al., *Sens. Actuators, B* **2020**, *306*, 127551.
[104] Z. Xu, Q. Wang, H. Zhangsun, S. Zhao, Y. Zhao, L. Wang, *Food Chem.* **2021**, *349*, 129202.
[105] D. Sheberla, J. C. Bachman, J. S. Elias, C. J. Sun, Y. Shao-Horn, M. Dincă, *Nat. Mater.* **2017**, *16*, 220.
[106] D. K. Ngyuen, I. M. Schepisi, F. Z. Amir, *Chem. Eng. J.* **2019**, *378*, 122150.
[107] K. Jayaramulu, et al., *Adv. Mater.* **2021**, *33*, 2004560.
[108] L. He, Y. Wang, Y. Xu, W. Cai, M. Zhu, H. Wang, *J. Alloys Compd.* **2021**, *876*, 160164.
[109] Y. Wan, B. Shen, X. Zhu, Z. Guo, *Chem. Phys. Mater.* **2024**, *3*, 388.
[110] Y. Jiao, et al., *J. Mater. Chem. A* **2017**, *5*, 1094.
[111] Y. Zhao, Z. Song, X. Li, Q. Sun, N. Cheng, S. Lawes, X. Sun, *Energy Storage Mater.* **2016**, *2*, 35.
[112] X. Chen, N. S. Villa, Y. Zhuang, L. Chen, T. Wang, Z. Li, T. Kong, *Adv. Energy Mater.* **2020**, *10*, 1902769.
[113] M. Wang, et al., *Adv. Funct. Mater.* **2020**, *30*, 2002664.
[114] B. Li, et al., *ACS Appl. Mater. Interf.* **2020**, *12*, 39444.
[115] Y.u Liu, S. Zheng, J. Ma, Y. Zhu, J. Wang, X. Feng, Z.-S. Wu, *J. Energy Chem.* **2021**, *63*, 514.
[116] R. Hosaka, R. Noji, *IFMBE Proc.* **2017**, *17*, 1061.
[117] B. Diao, C. Cong, F. Sun, H. Li, H. Zhang, X. Wang, M. Jin, S. Lim, X. Li, S.e Hyun Kim, *Chem. Eng. J.* **2024**, *500*, 156993.
[118] J. Cherusseri, D. Pandey, K. Sambath Kumar, J. Thomas, L. Zhai, *Nanoscale* **2020**, *12*, 17649.
[119] M.d R. Islam, O. Ichii, T. Nakamura, T. Irie, A. Shinohara, M.d A. Masum, Y. Otani, T. Namba, T. Chuluunbaatar, Y. H. A. Elewa, Y. Kon, *Animals* **2021**, *11*, 1768.
[120] W.-J. Song, J. Park, D. H. Kim, S. Bae, M.-J. Kwak, M. Shin, S. Kim, S. Choi, J.i-H. Jang, T. J. Shin, S.o Y. Kim, K. Seo, S. Park, *Adv. Energy Mater.* **2018**, *8*, 1702478.
[121] D. Zhou, Y. Yang, W. F. Rao, *3D Print. Addit. Manuf.* **2024**, *11*, 3.
[122] S. Chen, J. Qi, S. Fan, Z. Qiao, J. C. Yeo, C. T. Lim, *Adv. Healthcare Mater.* **2021**, *10*, 2100116.
[123] M. Yousuf, M. Garg, D. S. Arya, P. Singh, *IEEE Trans. Electron Devices* **2023**, 1338.
[124] H. Kim, Y. Kim, M. Mahmood, S. Kwon, F. Epps, Y. Rim, W. Yeo, *Biosens. Bioelectron.* **2021**, *173*, 112764.
[125] S. Ban, Y. J. Lee, S. Kwon, Y.-S. Kim, J. W. Chang, J.-H. Kim, W.-H. Yeo, *ACS Appl. Electron. Mater.* **2023**, *5*, 877.
[126] Y. T. Kwon, H. Kim, M. Mahmood, Y. S. Kim, C. Demolder, W. H. Yeo, *ACS Appl. Mater. Interf.* **2020**, *12*, 49398.
[127] N. Padmavathy, I. Chakraborty, A. Kumar, A. Roy, S. Bose, K. Chatterjee, *ACS Appl. Nano Mater.* **2022**, *5*, 237.
[128] Y. N. Liu, L. J. Feng, S. W. Bian, *ACS Appl. Electron. Mater.* **2022**, *4*, 4595.
[129] L. Jiang, L. Yuan, W. Wang, Q. Zhang, *Soft Sci.* **2021**, *1*, 5.
[130] L. Wang, et al., *J. Colloid Interface Sci.* **2022**, *616*, 326.
[131] Q. Zhao, J. Wang, S. Qu, Z. Gong, Y. Duan, L. Han, J. Wang, C. Wang, J. Tan, Q. Yuan, Y. Zhang, *ACS Nano* **2023**, *17*, 23115.
[132] M. M. Sabzehmeidani, M. Kazemzad, *Biomater. Res.* **2023**, *27*, 115
[133] F. Wang, X. Sun, Y. Zhou, X. Guo, J. Wu, X. Pan, Y. Cen, L. Pan, Y. Shi, *Biomed. Mater. Dev.* **2024**, *3*, 170.
[134] S. Ahmadi, K. Rahimizadeh, A. Shafiee, N. Rabiee, S. Iravani, *Process Biochem.* **2023**, *154*, 131.
[135] Y. Li, et al., *Nano Res.* **2021**, *14*, 2981.
[136] S. Biswas, A. Chowdhury, *Chem. Phys. Chem.* **2023**, *24*, 202200567.
[137] Y. Wang, et al., *ACS Appl. Energy Mater.* **2019**, *2*, 2063.

[138] X. Fang, B. Zong, S. Mao, *Nano-Micro Lett.* **2018**, *10*, 64.

[139] A. Zuliani, N. Khiar, C. Carrillo-Carrión, *Anal. Bioanal. Chem.* **2023**, *415*, 2005.

[140] P. S. Miri, N. Khosroshahi, M. D. Goudarzi, V. Safarifard, *Nanochem. Res.* **2021**, *6*, 2.

[141] M. Rizwan, V. Selvanathan, A. Rasool, M. A. U.r R. Qureshi, D. N. Iqbal, Q. Kanwal, S. S. Shafqat, T. Rasheed, M. Bilal, *Water, Air, Soil Pollut.* **2022**, *233*, 493.

[142] N. Jayababu, D. Kim, *Nano Energy* **2021**, *89*, 106355.

[143] T. Yan, et al., *Chem. Eng. J.* **2023**, *455*, 140779.

[144] M. S. Iyer, R. Ilangovan, *ACS Appl. Energy Mater.* **2023**, *6*, 3682.

[145] M. Al Sharabati, R. Sabouni, G. A. Husseini, *Nanomaterials* **2022**, *12*, 277.

[146] Q. He, F. Zhan, H. Wang, W. Xu, H. Wang, L. Chen, *Mater. Today Sustain.* **2022**, *17*, 100104.

[147] G. A. Leith, C. R. Martin, A. Mathur, P. Kittikhunnatham, K. C. Park, N. B. Shustova, *Adv. Energy Mater.* **2022**, *12*, 2100441.

[148] P. Ling, S. Cheng, N. Chen, C. Qian, F. Gao, *ACS Appl. Mater. Interf.* **2020**, *12*, 17185.

[149] J. Li, J. Yu, Z. Sun, H. Liu, X. Wang, *ACS Appl. Mater. Interf.* **2021**, *13*, 41753.

[150] B. Richard, K. Niyas, M. Ankitha, P. A. Rasheed, *ACS Appl. Nano Mater.* **2024**, *7*, 9585.

[151] J. E. D. S. Souza, G. P. D. Oliveira, J. Y. N. H. Alexandre, J. G. L. Neto, M. B. Sales, P. G. D. S. Junior, A. L. B. D. Oliveira, M. C. M. D. Souza, J. C. S. D. Santos, *Electrochem.* **2022**, *3*, 89.

[152] Z. Neisi, Z. Ansari-Asl, S. Jafarinejad-Farsangi, M. E. Tarzi, T. Sedaghat, V. Nobakht, *Colloids Surf., B* **2019**, *178*, 365.

Begüm Sarac continues her undergraduate education in Biomedical Engineering at Fatih Sultan Mehmet Vakıf University. She is working as a scholarship holder in the project 'Franz Diffusion Mathematical Modelling of Transdermal Bioactive Biomaterials' conducted by Dr. Ciftci. At the same time, Dr. Ciftci is also working on the project 'Wearable and implantable bioelectronic: Biosensing contact lens and applications' (published in "Chemical Engineering Journal") and 'Tissue engineering and biosensing applications of carbon-based nanomaterials (published in "Biomedical Engineering Advance"). The young researcher is involved in many studies under the supervision of Dr. Ciftci.

Seydanur Yücer continues her undergraduate education in Biomedical Engineering at Fatih Sultan Mehmet Vakıf University. She is working as a scholarship holder in the project 'Franz Diffusion Mathematical Modelling of Transdermal Bioactive Biomaterials' conducted by Dr. Ciftci. At the same time, Dr. Ciftci is also working on the project 'Wearable and implantable bioelectronic: Biosensing contact lens and applications' (published in "Chemical Engineering Journal") and 'Tissue engineering and biosensing applications of carbon-based nanomaterials (published in "Biomedical Engineering Advance"). The young researcher is involved in many studies under the supervision of Dr. Ciftci.

Fatih Ciftci is a researcher at Fatih Sultan Mehmet Vakıf University, Department of Biomedical Engineering (ISTANBUL, TURKEY). He obtained his Ph.D. in the field of bioengineering in 2021. His research interests include biomaterials, biopolymers, bioceramics, hard-soft tissue engineering applications, 3D transdermal tissue scaffold, MXene-MOF-Graphene nanomaterials, wearable technologies, biosensors, and rare diseases. He also has projects in the fields of artificial intelligence-machine learning, tissue engineering, and biotechnology, and his articles will be published in the near future. Dr. Ciftci actively participates in numerous national and international collaborative projects and serves as a reviewer for various scientific journals.