

Engineering of Functional Hybrid Nanocomposites for Renewable Energy Applications via Laser Ablation

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For my loving husband Morteza and my family

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"Gratitude is the wine for the soul. Fill your cup and let it overflow, for in the act of giving thanks, the soul finds its wings." - Rumi

Abstract

Carbon-based hybrid nanocomposites (HNCs) have increasingly gained prominence in the materials science community due to their widespread applications in advanced energy storage and conversion devices. Yet, current, and conventional methods to synthesize tailored HNC structures involve complex and multi-step processes that often require harsh chemical reagents. To address the majority of these shortcomings, this thesis proposes Laser Ablation Synthesis in Solution (LASiS) as a rapid, inexpensive, and facile technique for synthesis of Metal-Organic Framework (MOF)-derived and Metal Oxide/reduced Graphene Oxide (rGO) HNCs in an environmentally friendly fashion. These engineered composite nanomaterials show superior properties as (1) non-precious metal based electrocatalysts in electrochemical energy conversion systems, namely, Oxygen Reduction Reaction (ORR) at the cathode of Anion Exchange Membrane Fuel Cells (AEMFCs), and (2) high-performance electrode material comprised of reduced graphene oxide (rGO) interfaced with metal oxide nanostructures (rGO/MO_x) for Faradaic super capacitive (SC) energy storage devices. To that end, this thesis focuses on the synthesis-structure-property relations of these functional HNCs synthesized *via* LASiS with particular emphasis on high-performance supercapacitors and electrocatalysts. This, combined with precision, customization, and scalability, of current additive manufacturing technologies, allows three-dimensional (3D) printing of high performance SCs. Hence,, electrode printing is employed in optimizing 3D printed electrode designs, paving the way for advancements in energy storage technology.

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Chapter 1

Introduction to Electrochemical Energy Devices: Anion Exchange Membrane Fuel Cells and Supercapacitors

The search for sustainable energy solutions has led to significant advancements in electrochemical energy storage and conversion devices, notably anion exchange membrane fuel cells (AEMFCs) and supercapacitors (SCs). The challenges of durability, cost, and environmental impact are prevalent in both systems, which require innovative solutions. SCs, known for their higher energy density and ultrafast charge/discharge capabilities, have encountered limitations in charge storage capacity, often attributed to the use of carbonaceous materials as electrodes. Transition metal oxides, while offering higher specific capacity, lack certain desirable properties of carbonaceous materials. Recent research focuses on novel synthesis routes to create hybrid configurations, aiming to harness the advantages of both materials in electrochemical energy storage. In parallel, AEMFCs face challenges, including cost and environmental concerns associated with traditional catalysts such as platinum (Pt). Researchers are exploring catalyst synthesis to enhance the Oxygen Reduction Reaction

(ORR) at the cathode, seeking alternatives to Pt that are cost-effective and environmentally friendly.

1.1 Anion Exchange Membrane Fuel cells (AEM-FCs)

Fuel cells have increasingly established themselves as promising, clean, and efficient energy generation technology that converts the stored chemical energy in fuels directly to electric power and heat. Hence, new power generation and conversion technologies are key to addressing the global environmental impact of fossil fuels. Current fuel cells are mostly polymer exchange membrane fuel cells (*i.e.*, proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs)), alkaline fuel cells, solid oxide fuel cells, and molten carbonate fuel cells [8]. Except for the electrolyte, which defines their operating temperature, the overall design of these fuel cells is remarkably similar. AEMFCs (Figure 1.2) are electrochemical devices that convert chemical energy into electricity and produce water as a by-product. This chemical conversion occurs through two semi-redox reactions (Table 1.1) – namely, the oxygen reduction reaction (ORR) at the cathode (reaction (1)) and hydrogen oxidation reaction (HOR) at the anode (reaction (2)). The sluggish electrochemical reaction at the cathode is the rate-limiting step in AEMFCs during due to the high activation energy associated with the complex four-electron transfer process. To overcome this limitation, different nanoparticles (NPs)-based catalysts have been engineered to enhance the economic viability and efficiency of AEMFCs. Overall, Platinum (Pt)-based NPs are highly efficient catalysts for the complete four-electron transport pathway with significantly reduced overpotentials during the ORR process in alkaline fuel cells [50]. However, Pt is expensive and shows poor stability under the harsh alkaline conditions of electrochemical fuel cells. This highlights the need for inexpensive electrocatalysts that can easily replace Pt in AEMFCs. To that end, most recent studies have attempted to synthesize diverse classes of functional HNCs as ORR electrocatalysts. Despite the advantages of HNCs, no facile and direct method is available to date for their reliable and efficient synthesis.

Metal-Organic Frameworks (MOFs) represent a distinctive class of nanomaterials characterized by a crystalline structure comprising of metal nodes coordinated with organic linkers (Figure 1.1). This versatile framework has exceptional porosity, large surface areas, and tunable chemical functionalities. Hence, MOFs have found applications in diverse fields due to their unique properties, including gas and energy storage, electrocatalysis, sensing, drug delivery, and SCs [83, 87]. The distinctive structure of MOFs, with its tailored porosity and high density of transition metals, positions them as promising candidates for various electrochemical applications. In the context of AEMFCs, MOFs possess essential characteristics of non-precious metal electrocatalyst for the ORR at the cathode. Specifically, the extensive surface area and porosity of MOFs facilitate a high density of active sites for catalyzing the ORR, leading to enhanced electrocatalytic performance. The unique structural topologies of MOFs, influenced by the coordination number of metal centers and the symmetry of the organic linkers, also play a pivotal role in their electrocatalytic performance. Overall, MOFs offer an attractive alternative to conventional platinum-based catalysts, known for their effectiveness, but hindered by their prohibitive costs. Utilizing MOFs in AEMFCs allows one to achieve comparable or better electrocatalytic performance with earth-abundant and cost-effective materials, thus addressing the economic and environmental concerns associated with traditional catalysts.

Solvothermal / hydrothermal techniques are common for small scale synthesis of MOFs. These methods require dissolution of metal precursors and organic linkers in a solvent, which in turn poured into a sealed reaction vessel and placed inside a high-temperature oven to attain porous MOFs crystals. The common organic solvents used in these methods are N,N-Dimethylformamide (DMF), Methylene chloride (DCM), and N,N-Diethylformamide (DEF) with methanol, ethanol, or acetonitrile that are not only harmful to the human body but also leave unwanted interfacial residues on the final products that can be detrimental to their porous structure and interfacial functionalities. The synthesis temperature is also relatively high (220°C), and the crystallization time varies from hours to tens of days. Drawbacks associated with these techniques complicate high-volume production of high purity MOFs. To address the shortcomings of these conventional methods, this project uses a rapid, inexpensive, environmentally friendly, and high-performance technique, namely, LASiS to

synthesize MOF-derived HNCs. LASiS is not only a fast, dependable, and continuous experimental technique (without the need for constant monitoring), but also requires minimal equipment, and no harsh solvent compared to other synthesis approaches. In fact, one can realize the desired size, morphology, and functionality of synthesized nanomaterials by optimizing LASiS synthesis parameters and without use of unwanted surfactants. The superiority of this technique arises from creation of a high-energy liquid-confined laser-induced plasma that can create extreme temperatures and pressures that facilitate non-equilibrium reaction pathways that are otherwise inconceivable via traditional wet chemistry routes [104]. Thus, it is fair to regard LASiS as a novel and commercially viable process to synthesize MOFs and engineer HNCs in an efficient, reproducible, and cost-effective way. Details of the LASiS methodology will be presented in detail in the next chapters.

Platinum (Pt) is a noble and expensive metal that causes the final production cost of fuel cells to be increased by 45 to 75%. Therefore, the next logical step is to introduce new catalysts that are comparable to active but budget-friendly for Oxygen Reduction Reactions (ORR) at the cathode. Metal-Organic Frameworks (MOFs) have proven to be a promising candidate to be used as electrochemical catalysts in ORR owing to their large surface area and porosity, as well as a high density of transition metals[87]. MOFs belong to a unique hybrid nanomaterial class that can be used for numerous applications such as gas and energy storage, electrocatalysis, supercapacitors, sensing, and drug delivery[28]. Depending on the application, MOFs can be synthesized through “the conventional methods” such as solvothermal/hydrothermal techniques or, as demonstrated recently by our research group *via* Laser Ablation Synthesis in Solution-Galvanic Replacement Reaction technique (LASiS-GRR) [87]. There are several challenges associated with the synthesis of MOF structures *via* conventional methods which make the synthesis an energy-inefficient and timely process. In contrast, LASiS technology is an inexpensive, simple, and environment-friendly experimental set-up that requires minimal manual operation in the synthesis and fabrication of MOFs. Anticipated contributions include the development and validation of a cost-effective LASiS synthesis method for advanced HNC structures, offering immediate applications in ORR catalysis and Faradaic supercapacitive devices. The study further aims to create a robust

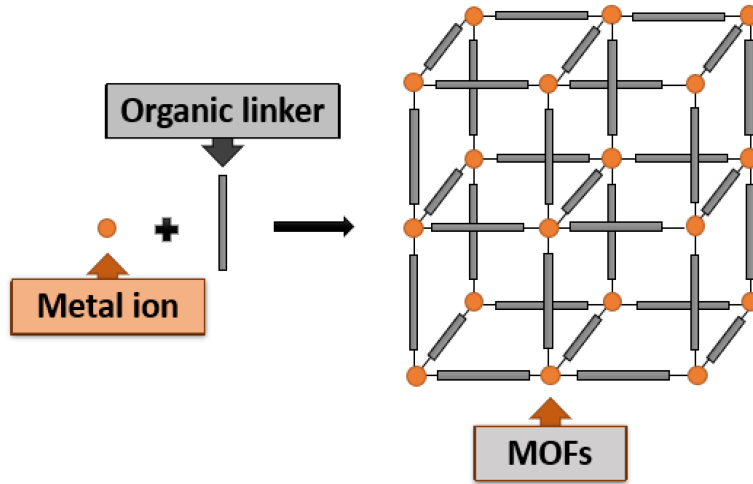


Figure 1.1: Schematic diagram of the synthesis procedure for MOFs.

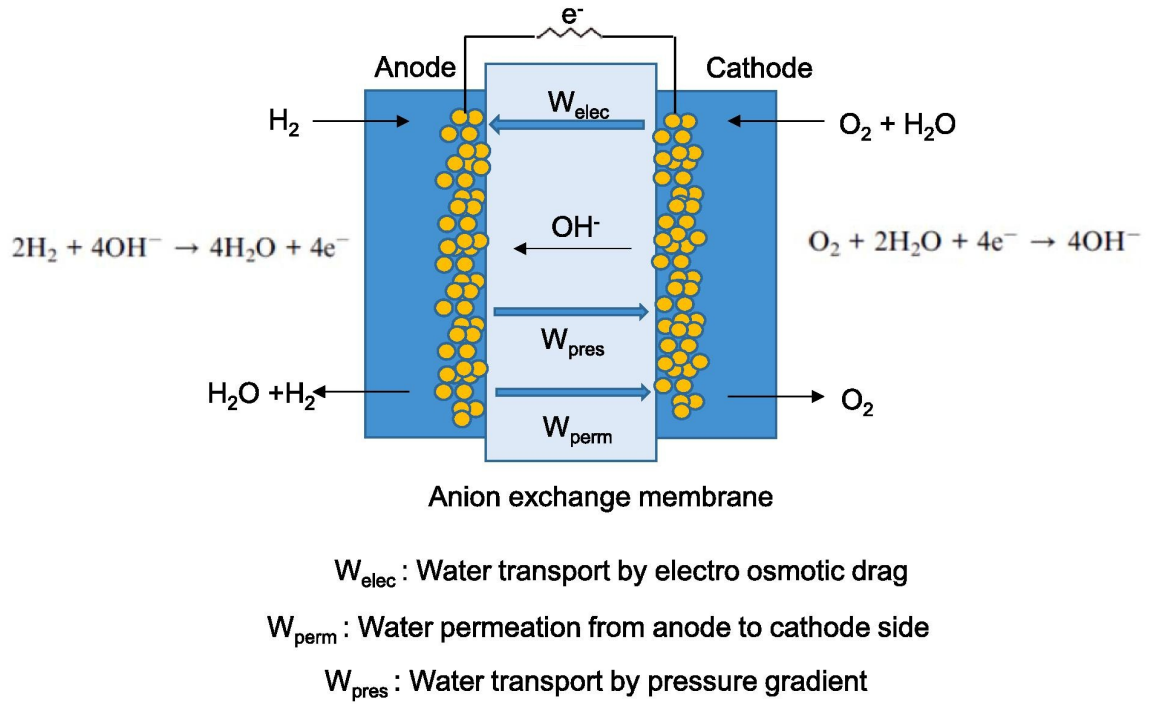


Figure 1.2: Illustration of alkaline anion exchange membrane fuel cell.

Table 1.1: Anode, Cathode, and Overall Cell Reaction of AEMFCs

Anode Reaction (1)	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
Cathode Reaction (2)	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall Cell Reaction (3)	$2H_2 + O_2 \rightarrow 2H_2O$

dataset and ML model, streamlining the selection of MOFs and advancing insights into their electrochemical performance, thus paving the way for future advancements in the field.

1.2 Energy Storage Devices; Supercapacitors

The escalating demand for compact electrochemical energy storage devices, propelled by the ubiquity of portable electronics and autonomous gadgets, has led to the widespread utilization of batteries and SCs. Batteries, the predominant energy storage devices, transform chemical energy into electrical energy through faradaic processes within cells that comprise anodes, cathodes, separators, and electrolytes. Conversely, SCs, resembling capacitors with heightened charge storage capacity, leverage porous electrodes and dielectrics for substantial capacitance. Figure 1.3 illustrates the operational principle of batteries, elucidating the faradaic process of converting chemical energy to electrical energy [129].

SCs exist in three main types: electrochemical double layer (EDL) capacitors, pseudocapacitors (PC), and hybrid SCs. EDL capacitors utilize electrochemical double layers in the electrolyte to control the energy density, often employing carbonous or graphitic electrodes. Pseudocapacitors engage in fast and reversible faradaic reactions at the electrode surface, achieving higher energy densities than EDL capacitors because of engineered materials with high surface redox site concentrations, such as metals and metal oxides. The third type, hybrid supercapacitors, combines faradaic and non-faradaic processes for charge storage, enhancing electrochemical performance through EDLC and pseudocapacitive materials. Figure 1.4 shows the three main types of supercapacitors based on charge storage mechanisms and electrode materials [22].

The structural design of the electrodes significantly influences the performance of SCs. Carbon-based supercapacitors, known for their excellent thermal and electrochemical stability, affordability, proper electrical conductivity, adjustable porosity, and optimal active sites, are the most popular EDLC supercapacitors. For high-capacitance SCs, carbon electrodes with an adjustable pore structure, a sufficiently high specific surface area, and abundant surface functional groups are essential. Electrolytes also play a crucial role, requiring enhanced surface chemistry in carbon materials for high-operating voltage SCs.

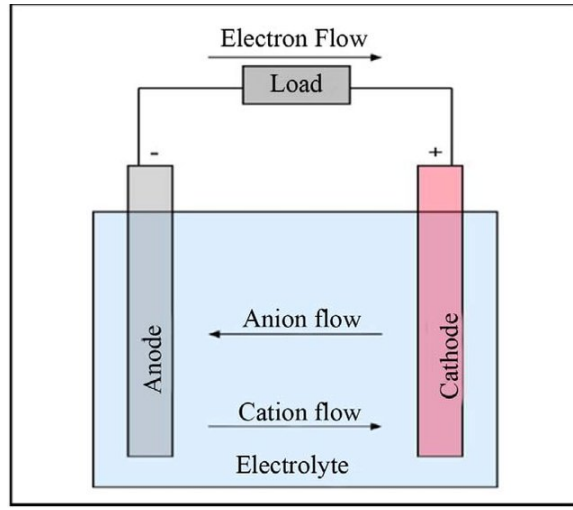


Figure 1.3: Battery Operation Principle, how they work?

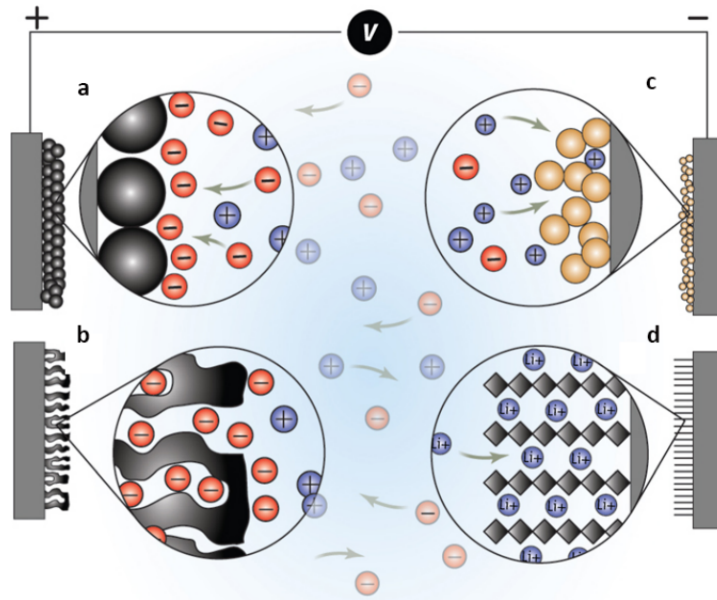


Figure 1.4: Illustration of different mechanisms of supercapacitors. Double-layer capacitance mechanisms include of (a) carbon particles or (b) porous carbon. Pseudocapacitive mechanisms include (c) redox and (d) intercalation pseudocapacitance.

Furthermore, achieving high-energy SCs requires meticulous cell design and manufacturing. Therefore, it is essential to study the advances in SC electrode materials, electrolytes, and design and manufacturing technologies, providing insights into the evolving landscape of electrochemical energy storage devices. Figure 1.5 delineates various types of supercapacitors based on charge storage mechanisms and electrode materials, emphasizing the impact of electrode structural design.

1.3 Supercapacitors: Electrode Material

The material used to prepare the electrodes significantly influences the performance of supercapacitors (SCs). Both the design and the inherent characteristics of the electrode materials play a crucial role in determining SC performance [60] as the capacitance of a supercapacitor increases in proportion to the surface area of the electrodes. Hence, the porosity of the electrodes emerges as a crucial property. Porous materials, which offer a higher surface area per unit volume, contribute to increased capacitance in SC electrodes. The key features of an effective SC electrode material include high electronic conductivity, low electrical resistance, cost-effectiveness, mechanical strength, and proper thermal stability. Carbon stands out as the most common material for SC electrodes due to its excellent electronic/ionic conductivity, low electrical resistance, abundance, thermal stability, corrosion resistance, and affordability [3]. Ongoing efforts to enhance accessible pores in porous carbon have yielded various carbon-based electrodes. In addition, metal oxides, metal-organic frameworks, and conducting polymers serve as typical electrode materials, boasting a high specific capacitance compared to their carbon counterparts.

1.3.1 Activated Carbon

In supercapacitors, activated carbon stands out as the most widely used electrode material [92]. This type of carbon undergoes processing to create fine pores, resulting in a higher surface area. Various activation procedures exist, often using raw carbonaceous biomass materials such as wood and coal. The physical activation process involves raising the material to elevated temperatures (700 °C - 1200 °C) and in turn processing them in the presence

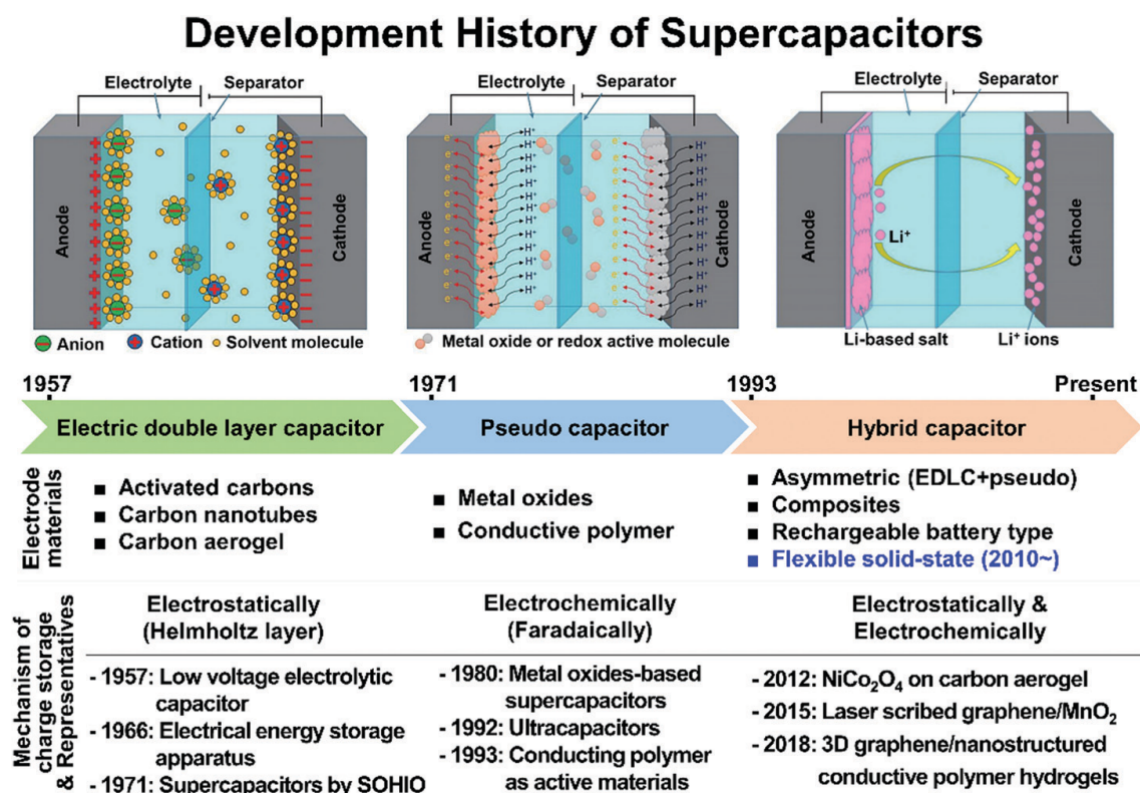


Figure 1.5: Development of SCs based on different charge Storage mechanism and electrode materials

of oxidizing gases such as steam and CO_2 [77]. On the other hand, the chemical activation process treats the carbon precursor at a lower temperature with chemicals such as alkalis and alkaline earth metals. Activated carbon electrodes typically feature micropores (less than 1 nm), mesopores (1 nm - 40 nm), and macropores (greater than 40 nm) [3]. The electrostatic storage of charges on the activated carbon leads to double-layer capacitance.

Activated carbon has drawbacks, including inferior mechanical properties and the need for metal current collectors. Activated carbon inks with precise composition and rheology are necessary to meet the requirements of printed supercapacitors (SCs). For example, in one study, activated carbon particles were combined with PTFE binders in ethylene glycol fixed with a surfactant to develop an inkjet ink successfully [94]. The resulting activated carbon ink was 3D printed using an inkjet printing process on gold current collectors, yielding SCs with outstanding capacitive behavior across a wide potential range of 2.5 V and a cell capacitance of $2.1 \text{ mF}\cdot\text{cm}^{-2}$ (Figure 1.6(a)). Another study highlighted an SC ink containing activated carbon dispersed in DI- H_2O and matte media as a binder, exhibiting capacitances of $0.51 \text{ F}\cdot\text{cm}^{-2}$ at 10 mV s^{-1} [64]. Recent research on a 3D-printed SC based on porous activated carbon from packaging waste material demonstrated that the printed design could achieve a high capacitance of $328.95 \text{ mF}/\text{cm}^{-2}$ at 2.5 mA [59]. The solid-state SC, fabricated by extrusion-based 3D printing, included a high loading of activated porous carbon to enhance the capacitance (Figure 1.6(b)).

1.3.2 Carbon nanotubes (CNT)

Since the surface area of the electrode plays a significant role in the capacitance values, research have shown that pore size distribution also plays an essential part in the effectiveness of a material utilized as SC electrodes. Pores with sizes smaller than electrolyte ion sizes will not engage in the electrochemical process. Due to the inherently broad pore size distribution, not all pores in activated carbon can participate in the charge storage. CNTs, on the other hand, have highly porous and interlinked pore sizes, providing greater access for the electrolyte ions and, hence, better utilization of electrode surface area. Due to better electrolyte ion transport into the highly porous interlinked network, SCs containing CNTs have a lower equivalent series resistance than activated carbon SCs [59].

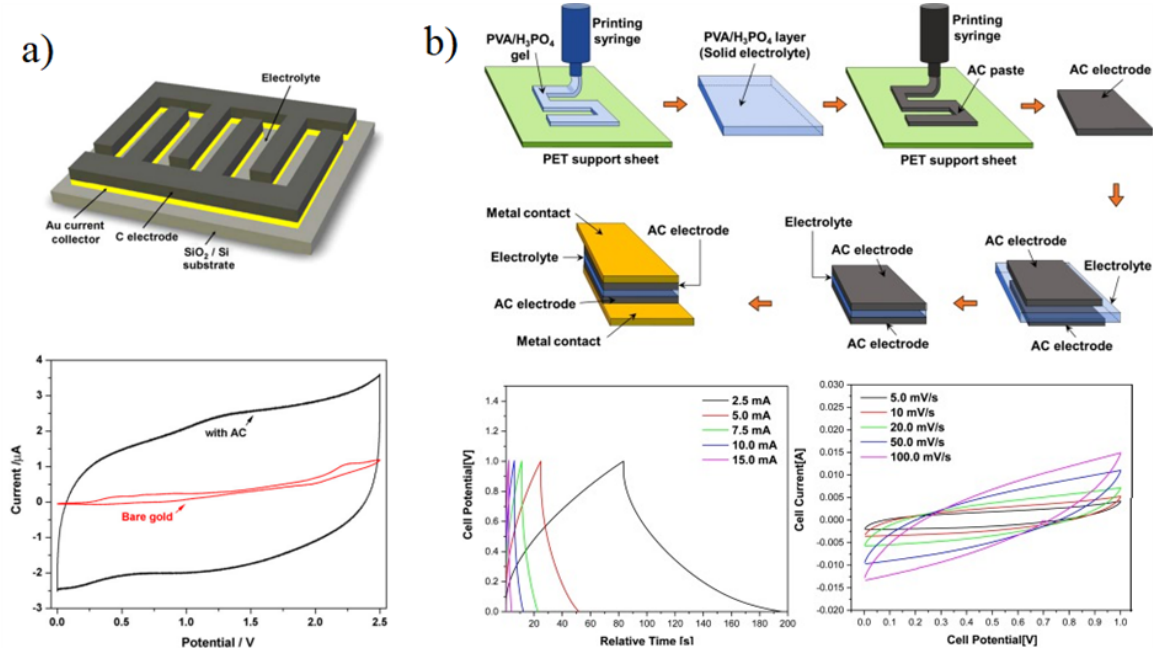


Figure 1.6: a) Illustration of micro-supercapacitor on gold current collector layer and CV plots of the coated and uncoated with activated carbon (AC) electrodes at 100 mV s^{-2} , and b) Illustration of the SC fabrication process, Galvanostatic CD and CV curves at different current and voltage scan rates.

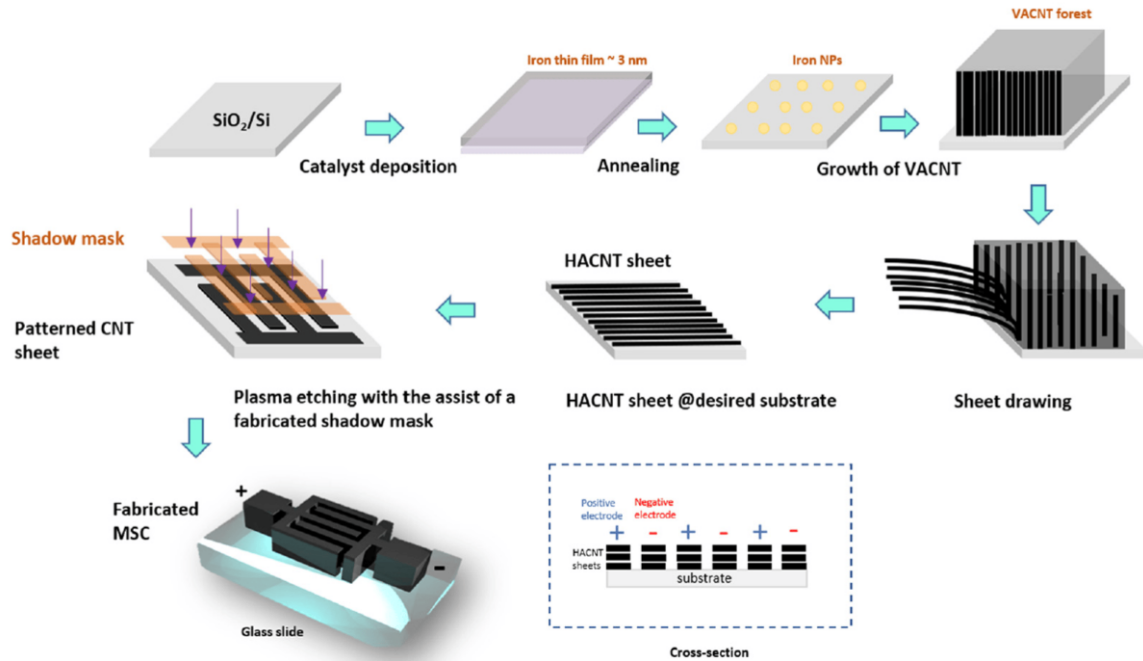


Figure 1.7: Workflow diagram of the engineering of significantly aligned CNTs.

Based on their structure, CNTs are classified as single-walled and multi-walled CNTs with distinctive pore sizes. This has led a new era in developing carbon-derived SC electrodes. These materials outperform activated carbon in terms of electrical conductivity, mechanical stability, and chemical stability. They are prepared through the controlled decomposition of specific hydrocarbons, such as the catalytic degradation of acetylene used to prepare a CNT. This specific control allows the manipulation of process parameters to attain the desired nanostructure. Although, in theory, CNTs benefit from a higher specific capacitance compared to activated carbon, practical CNT SC shows slightly higher or, in some cases, lower specific capacitance [15]. However, different manufacturing techniques could improve the specific capacitance of CNT SCs. Since CNTs, despite their distinctive structure, do not necessarily display improved specific capacitances, composited electrodes with CNTs and other material show higher specific capacitance. Different CNT inks have also been formulated and investigated for printed SCs. In one case, an interdigitated electrode planar design was used to create a high energy density extremely thin and aligned CNT sheet SC (Figure 1.7). The device contains 50 layers and a total low thickness of 300 nm, while its energy density is 10.5 mWh/cm³ and contains a power density of 19 W/cm³ [32].

1.3.3 Carbon Aerogels, and Hydrogels with Conducting Polymers

Aerogels, distinctive gel-shaped materials, undergo a process where the liquid part is removed and replaced with air. Carbon aerogels are formed through the pyrolysis and carbonization of organic aerogels, such as resorcinol-formaldehyde aerogels, in inert gases (N₂, He, or Ar) at temperatures exceeding 600°C [32]. These aerogels exhibit a mesoporous structure with adjustable pore size distribution during manufacturing. Their monolithic structures, characterized by extreme lightweightness, eliminate the need for electrode binders, resulting in lower Equivalent Series resistance. Consequently, carbon aerogels are an excellent choice for SC electrode material due to their low density, high surface area, mesoporous and monolithic structure, and high conductivity. Experimental studies have demonstrated proper specific capacitance, but the expensive process of supercritical gel drying, and the environmental harm associated with standard precursors (resorcinol and phenol) currently limit their use in commercially available SCs. Another promising category of nanostructured

carbon materials includes carbon nanofoams and carbon nano coils, often used as electrode materials combined with metal oxides to enhance conductivity and reduce manufacturing costs.

Aerogels have recently shown promise in 3D printed energy storage applications, with graphene aerogels gaining significant attention. Their large specific surface area for ion accessibility, controllable porosity, and unique mechanical behaviors makes them attractive. Scientists have developed gel-based inks from viscoelastic functional materials exhibiting non-Newtonian shear-thinning characteristics to facilitate direct ink writing of these aerogels. For extrusion-based direct writing, an extrudable graphene oxide-based composite aerogel ink was developed [96]. This ink, composed of graphene oxide, silica fillers, catalysts, and graphene nanoplatelets, aimed to improve electrical conductivity and decrease ink resistance without compromising surface area. The key challenge was maintaining adequate wetness in ink during the printing and gelation process and converting the 3D-printed design into an aerogel. The aerogel ink developed, extruded through a micron size nozzle in an isooctane bath to prevent gel collapse (Figure 1.8), transformed into a porous aerogel design through gelation, supercritical drying and pyrolysis, followed by HF acid etching of silica. The resulting symmetric supercapacitor, printed using direct ink writing, exhibited a capacitance of 4.76 F/g at a current density of 0.4 A/g, retaining over 60 percent of capacitance at an increased current density of 8 A/g [139]. Another study explored 3D printing and polymer self-assembly to develop a super-elastic graphene aerogel electrode coated with polypyrrole (PPy) organic polymer, as shown in Figure 1.9 [97]. The PPy/graphene aerogel electrode displayed a high specific capacitance of 395 F/g, along with good mechanical behavior due to adjustable periodic fine pores, uniform deposition, and PPy adhesion.

However, hydrogels have garnered interest for additive manufacturing of SCs due to their flexibility, stretchability, availability, and biocompatibility. Hydrogels containing conducting polymers present a compelling material that combines the advantages of both hydrogels and conducting polymers. Researchers employed a gelator, amino trimethylene phosphonic acid (ATMP), and a dopant to create a hierarchically nanostructured polyaniline (PANI) hydrogel [97], illustrated in Figure 1.10. 3D printing of ammonium persulfate and aniline ink droplets on the same printing site facilitated rapid hydrogel synthesis. The resulting 3D conductive

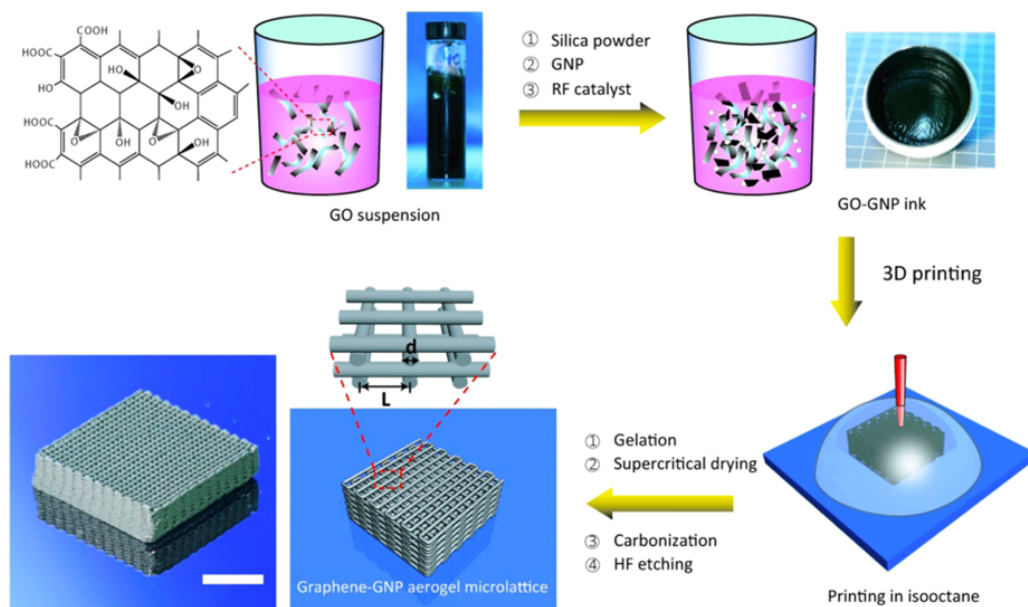


Figure 1.8: Illustration of a 3D DIW fabrication printing technology.

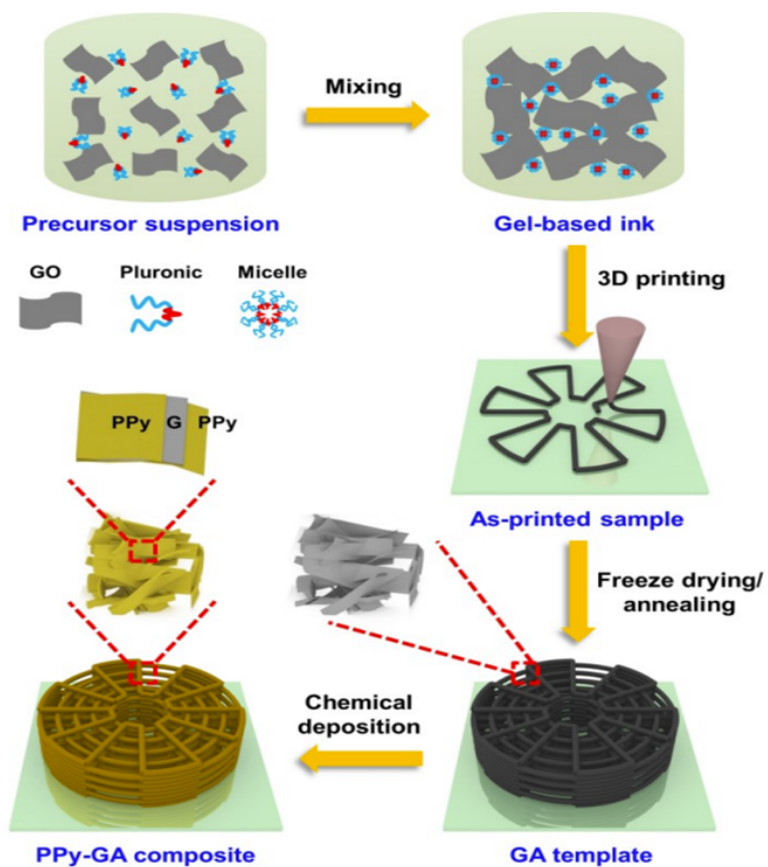


Figure 1.9: 3D hierarchical PPy and graphene aerogel composites printing technology.

network design improved electron transport and improved the elasticity of the polymer. At a current density of 0.2 A/g, the printed PANi hydrogel electrode achieved a capacitance of approximately 422 F/g, which improved to around 240 F/g at a current density of 10 A/g.

1.3.4 Graphene

Graphene, a single layer of graphite and one of the carbon allotropes boasts remarkable properties, including a large specific surface area, excellent electrical conductivity, and chemical and thermal stability, making it a promising candidate for electrode material applications. A single graphene sheet has a surface area of 2630 m²/g, significantly exceeding activated carbons commonly used in SCs. Furthermore, graphene finds use in flexible SCs. In fact, experimental studies have suggested the possibility of achieving a high energy density up to 136 Wh/kg at 80°C, upon taking full advantage of graphene's large surface area. Graphene can leverage its mechanical strength as a substrate in supercapacitor electrodes, combined with metal oxides and conducting polymers [65].

Various methods are employed to produce graphene, with solution-based and chemical exfoliation standing out as standard procedures for preparing printable graphene inks. Through polymer stabilization and solvent exchange procedures, a straightforward and efficient process yields stable graphene inks with high concentrations, suitable for cost-effective inkjet printing techniques. SCs produced using this method demonstrated an aerial capacitance close to 0.59 mF.cm⁻². Figure 1.11 illustrates the successful fabrication of a quasi-solid-state micro-SC using graphene film and polyvinyl alcohol/H₃PO₄, highlighting superior electrochemical performance [111].

1.3.5 Metal Oxides

Metal oxides utilized in electrode materials can induce pseudo capacitance due to the faradaic charge storage process of the metal. They exhibit significantly higher specific capacitance compared to carbon-based material electrodes, making them ideal for SCs with high energy density. Among the commonly used metal oxides in SCs, ruthenium oxide stands out, demonstrating a specific capacitance as impressive as 788 F/g [?]. Combining metal

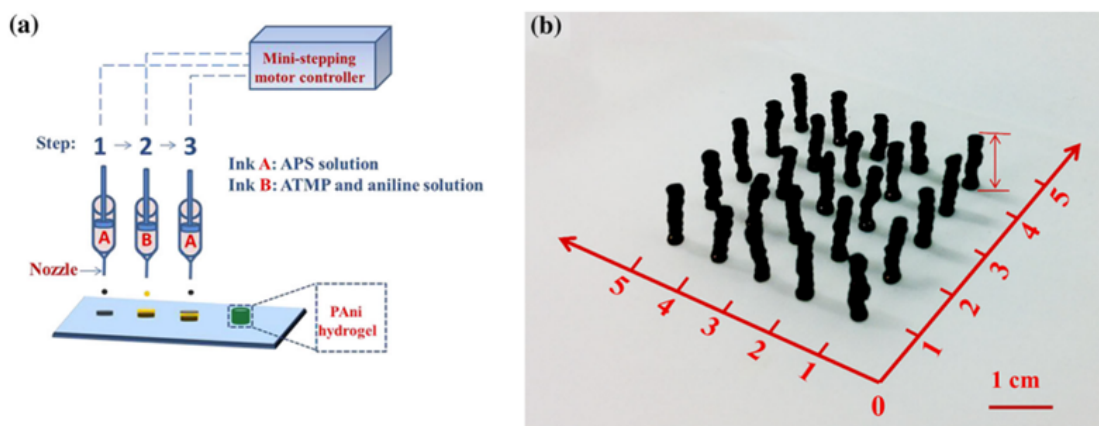


Figure 1.10: Illustration of PANi hydrogel patterns fabricated by 3D printing. a) 3D printing of the PANi hydrogel. b) array of printed PANi hydrogel with 15 layers.

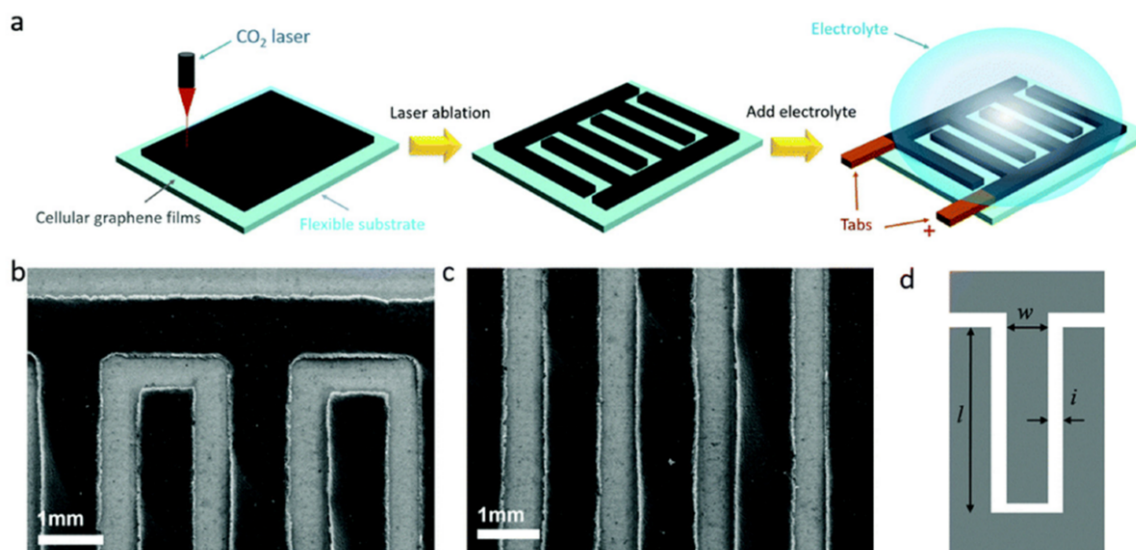


Figure 1.11: a) Illustration of a cellular graphene-based micro-supercapacitor fabrication process; (b,c) SEM images of the top view of micro-electrodes; and d) pattern dimension.

oxides with carbon-based materials for electrodes is prevalent, leveraging the high specific capacitance from the metal oxide side and the robust electrical conductivity of the carbon part. Manganese oxide (MnO_2), nickel oxide (NiO_2), and iridium oxide (IrO_2) are among the metal oxides regularly employed in conjunction with carbon materials for SC applications. Due to the low electrical conductivity of metal oxides, the use of binders and conductive additives is typically necessary when formulating metal-based inks.

1.3.6 Metal organic frameworks (MOFs) and covalent organic frameworks (COFs)

The exceptional features of metal-organic frameworks (MOFs), such as high porosity, controlled pore size, varied architectures, chemical stability, and adjustable chemical compositions, position them as a promising category of supercapacitor (SC) electrode materials. MOFs can exhibit high specific surface areas, reaching up to $46,000 \text{ m}^2 \text{ g}^{-1}$, indicating significant potential for energy storage applications. For instance, zirconium MOFs have demonstrated a high capacitance of around 5.09 mF cm^{-2} , which remained stable after at least 10,000 charge-and-discharge cycles [21]. Another class of material, namely, covalent organic frameworks (COFs), synthesized first by Yaghi et al., features porous organic structures connected by covalent bonds [24]. Similar to MOFs, COFs offer tunable pore sizes, large surface areas, and excellent flexibility, making them viable for energy storage systems. Researchers have reported SC electrodes composed of thin COF sheets, exhibiting a superior areal capacitance of 1600 mF cm^{-2} (gravimetric 169 F g^{-1}). Both MOFs and COFs present attractive qualities for application in printed SCs, owing to their organic and soluble characteristics.

Table 1.2. provides a summary of electrode materials and their specific capacitances in various specific electrolytes.

1.4 An Overview of Additive Manufacturing and its Significance

Metal oxides utilized in electrode materials can induce pseudo capacitance due to the faradaic charge storage process of the metal. They exhibit significantly higher specific capacitance compared to carbon-based material electrodes, making them ideal for SCs with high energy density. Among the commonly used metal oxides in SCs, ruthenium oxide stands out, demonstrating a specific capacitance as impressive as 788 F/g [80]. Combining metal oxides with carbon-based materials for electrodes is prevalent, leveraging the high specific capacitance from the metal oxide side and the robust electrical conductivity of the carbon part. Manganese oxide (MnO_2), nickel oxide (NiO_2), and iridium oxide (IrO_2) are among the metal oxides regularly employed in conjunction with carbon materials for SC applications. Due to the low electrical conductivity of metal oxides, the use of binders and conductive additives is typically necessary when formulating metal-based inks.

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Both MOFs and COFs present attractive qualities for application in printed SCs, owing to their organic and soluble characteristics.

To this point, a brief summary of the diverse material and methodologies employed in fabrication of electronic systems, often with a substantial carbon footprint has been given. In addition, waste generation during production is notable, and the manufacturing process is time intensive. In pursuit of cost-effective and flexible alternatives to traditional manufacturing processes, inkjet printing has emerged as a viable alternative in the realm of printed electronics. However, the quality of the final product and the speed of manufacturing limits the use of inkjet printing in high throughput manufacturing of electronic devices. In addition, the compatibility of inkjet printing with other manufacturing steps required for final product assembly, remains a challenge. Although manufacturing of electronic circuits by 3D printing is possible, current designs are nascent and lack the desired complexity. To transition 3D printing technology from the laboratory settings to industrial applications, especially for higher throughput production, the development of more intricate and sophisticated designs is imperative. Presently, manufacture of basic on/off switches is common, limiting their use in analog devices. This thesis advocates an integrative approach to printed supercapacitor (SC) fabrication, device assembly for 3D printed SC systems, and printed electrode manufacturing, all within a single and highly efficient 3D printing process. The proposed 3D printing method aims to offer economic advantages in terms of energy storage and reduced carbon footprint. The potential benefits include reduced production waste, cost, time, and energy consumption, as well as improved device performance.

It what follows the application of 3D printing technology as an integrated method that couples circuit board fabrication, electronic component assembly for electronic systems, and supercapacitor manufacturing using inkjet printing is given, with particular emphasis on understanding and leveraging 3D printing methods and technologies for manufacturing 3D printed flexible electronics at industrial scale, moving beyond the realm of experimental prototypes. Additionally, the chapter reviews various 3D printing methods, materials, and technologies, outlining their current status and functionality. The potential for future studies and growth in using these methods for the manufacture of advanced 3D printed electronics is highlighted. By bridging the gap between theory and practical application, this chapter

Table 1.2: SC Electrode Materials and their corresponding Specific Capacitances

Electrode materials	Electrolyte	Specific Capacitance (F/g)
Activated Carbon	Aqueous (NaOH/KOH)	200-400
Carbon nanotubes	Aqueous (NaOH/KOH)	20-180
Carbon Aerogels	Aqueous (NaOH/KOH)	40-200
Graphite reduced Graphene oxide (rGO)	Tetraethylammonium tetrafluoroborate (Et ₄ NBF ₄)	10-150
Manganese oxide (MnO ₂)	K ₂ SO ₄	261
Ruthenium oxide (RuO ₂)	H ₂ SO ₄	650-735
Polypyrrole (PPy)	Aqueous Electrolyte	40-588
Polyaniline (PANI)	Aqueous Electrolyte	120-1530
MOF/COF	Aqueous (NaOH/KOH)	169

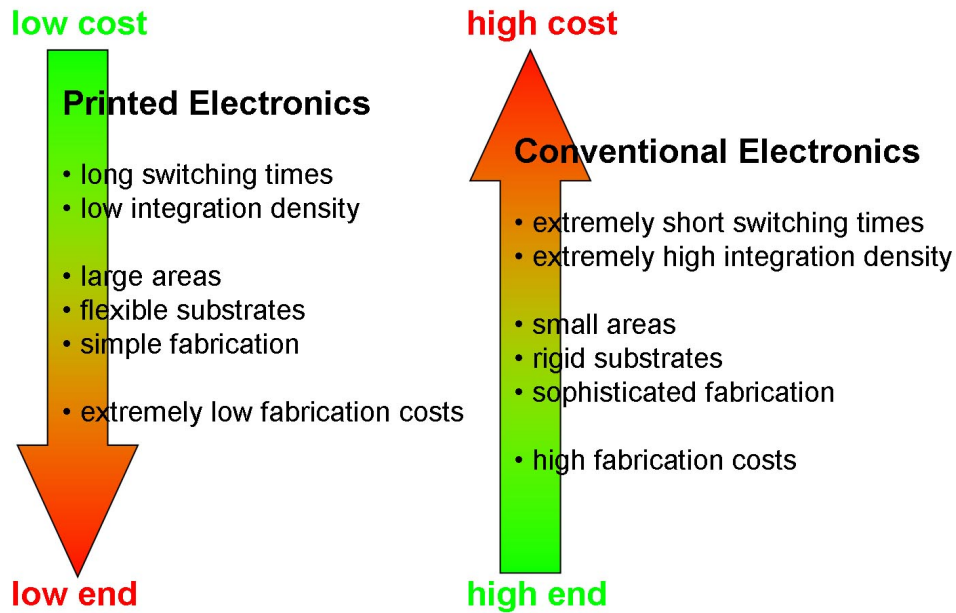


Figure 1.12: A comparison between printed and conventional electronics as complementary technologies [Source: Institute of Print and Media Technology, Chemnitz University of Technology by Heiko Kempa].

aims to contribute to the evolution of 3D printing technology for industrial-scale production of SCs.

1.5 Additive Manufacturing Technology

The additive manufacturing (AM) process leads to the generation of 3D devices/designs through the stacking of deposited material (metal or plastics, etc.) in layers [29]. This process first emerged in 1987 for Rapid Prototyping (RP) [130, 95]. In that process, digital designs were generated by CAD software, and in turn fabricated by the stereolithography (SL) process where thin layers of a viscous polymer are compressed into a light-sensitive solid that in turn is exposed to ultraviolet (UV) radiation. Around the mid-1990s, access to sophisticated CAD tools allowed 3D printing/fabrication started to grow. By Starting in 2000, additive manufacturing gained more interest as it proved successful in producing a 3D-printed prototype of a functioning kidney, that in turn was transplanted in patients. In less than a decade, high-definition (HD) color 3D printers emerged, and a new era of commercialization started, and access to AM significantly grew[10]. AM process continues to develop in electronic devices and other industries such as , medical technology, the automotive industry, etc. Figure 1.15 shows the first 3D-printed car made in 2015. This 3D-printed car resulted from a joint venture between Local Motors and Oak Ridge National Laboratory (ORNL) [34]. Figure 1.16 displays the predicted market share for the fields of 3D printed, flexible, and organic electronics in 2018, with a considerable overlap with each other.

The development of AM technology continues to play an essential role in rapid manufacturing in a broad range of industries. The broad applicability of AM is due to the advantages that it offers in comparison to traditional manufacturing techniques. These include low capital cost, cost effectiveness, low waste and rapid prototyping and manufacture. To that end, the electronic industry is making significant use of AM. The comparison between printed and conventional electronics as complementary technologies can be seen in Figure 1.12. Printed electronics are incredibly economical, facile, and efficient, while conventional electronics have more complex and require sophisticated designs. The

electronics industry is a billion-dollar market with fast growth. The main factors that play a key role in electronic system manufacturing are the search for economical and cost-effective manufacturing procedures, the reduction of the carbon footprint and the search for a low fabrication time [48]. Energy-efficient routes, low production time, and environmentally friendly procedures have led to widespread use of AM [12]. To that end, approaches to integrate a branch of additive manufacturing, namely, 3D printing, and electronics system manufacturing is on the rise. These techniques include inkjet printing using liquid conductive nanoparticle (NP) inks to print three-dimensional printed patterns. Although inkjet printing has proven to be a desirable route for producing electronics, significant challenges have to be resolved before its widespread use in the electronic industry. These include the rheology of the ink, clogging, and aggregation [66].

A prediction by Yole Development in February 2014 showed that the printed and flexible electronics industry would be close to one billion US dollars by the end of 2020, giving a compound annual growth rate (CAGR) of 27%. In this regard, Figure 1.13 shows that functional printing will capture 89% of the market share by 2020 [110]. If this prediction is accurate, extensive possibilities for printing electronics with widespread applicability in a broad range of industries such as healthcare, consumer electronic exists. Specifically, the emergence of flexible printed electronics will lead to the growth of sensors, smart textiles, and circuit domains. The traditional method of designing electronic devices involves selective removal of material from the original template. The process that included preprogrammed electronic models was costly due to material (quantity, price), equipment, and complex and time-consuming procedures, such as washing, cleaning, and disposal. This time-consuming process also requires multiple chemical processing steps [23], hence, it is not environmentally friendly. To that end, 3D and 2D printing has opened new avenues for electronics fabrication. 2D printing employed inkjet and aerosol [136] printing to manufacture electronics with homogeneous structures on flat surfaces, while 3D printing is capable of repeating a 2D digital design (pilling) created by CAD software and repeat it to produce the desired 3D structure [117, 30]. Various 3D printing methods, such as binder-inkjet, powder-bed-based printing, and extrusion-based printing methods, were adapted to other 2D printing methods to allow simultaneous manufacture of multi-functional electronics. However, these

advanced technique have materials, dimensions, production volume and feature resolution limitation. Overcoming these limitations should allow fast fabrication processes for high-resolution products. Hence, 3D printing of electronics can go beyond being a prototyping technique and adopted for mass production [79, 63]. This will have an enormous impact on a 40 billion dollars industry according to IDTechEx (Figure 1.14).

1.6 Summary

The quest for efficient materials and methods for printed SCs has led to various choices, each with unique advantages and considerations. Carbon-based materials, particularly activated carbon, and graphene, stand out because of their high specific surface areas, excellent electrical conductivity, and thermal stability. Use of activated carbon inks and graphene-based composites has facilitated cost-effective and printable solutions, offering promising results in terms of capacitance. Metal oxides, such as ruthenium oxide, manganese oxide, nickel oxide, and iridium oxide, contribute to pseudocapacitance, offering high specific capacitance and enhancing the energy density of supercapacitors. Additionally, metallic, and bi-metallic MOFs exhibit high porosity, tunable pore sizes, and promising capacitance values, positioning them as attractive candidates for printed supercapacitors, especially considering their organic and soluble features. Therefore, combining metal oxides and metallic MOFs with carbon materials in a composite format harnesses both strengths, overcoming the low electrical conductivity of the metal component and improving the capacitive behavior of the final product as a hybrid nanocomposite. Methods such as 3D printing, inkjet printing, and direct ink writing play a crucial role in shaping the final characteristics of SCs. Optimization of these methods, along with continuous advances in electrode materials, holds the key to unlocking the full potential of printed SCs for diverse energy storage applications.

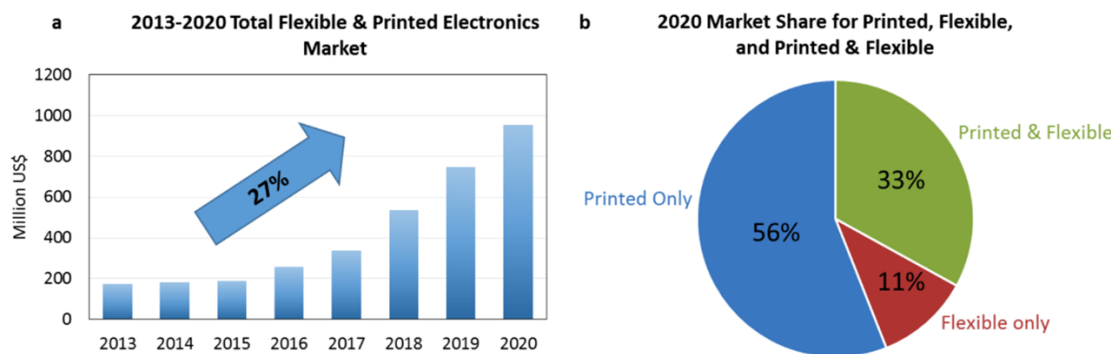


Figure 1.13: (a) 2013-2020 Flexible & Printed Electronics Market, (b) 2020 Market Share for Printed, Flexible, and Printed and Flexible. Adapted from Materials & Equipment for Printed and Flexible Electronics, Yole Développement, 2014.

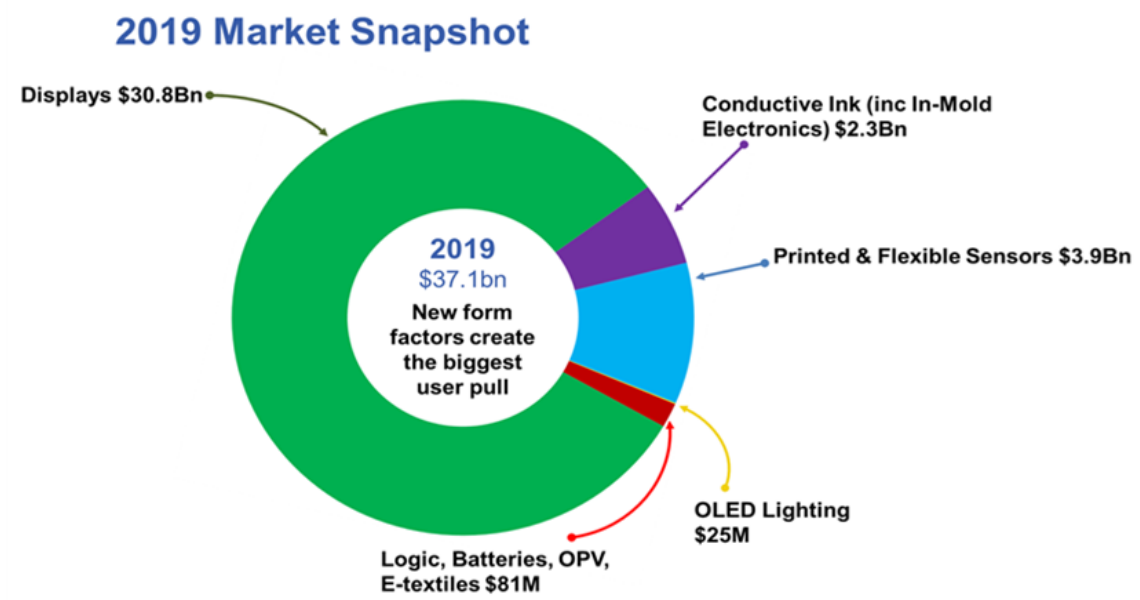


Figure 1.14: A snapshot of the printed, organic, and flexible electronics industry in 2019. Source: IDTechEx.



Figure 1.15: The First 3D Printed Car in the world, Strati.

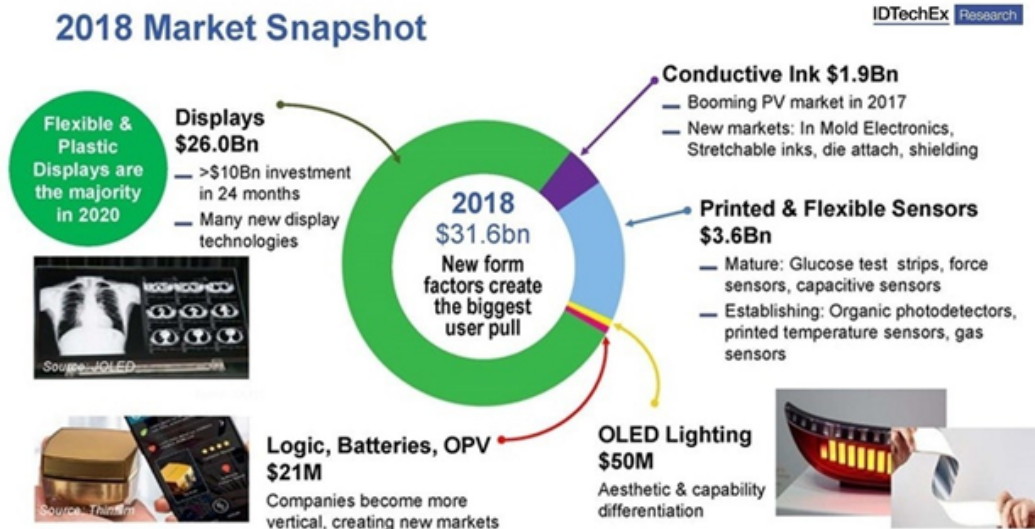


Figure 1.16: Market of Printed, Flexible and Organic Electronics in 2018. Source: IDTechEx.

Chapter 2

3D Printed Interdigitated Supercapacitor Using Reduced Graphene Oxide-MnO_x/Mn₃O₄ Based Electrodes

This chapter is based on submitted and published article: *"3D printed interdigitated supercapacitor using reduced graphene oxide-MnO_x/Mn₃O₄ based electrodes"* by Mahshid Mokhtarnejad, Erick. L Ribeiro, Dibyunde Mukherjee, and Bamin Khomami.
DOI: 10.1039/D2RA02009B

In this chapter, hybrid nanocomposites (HNCs) based on manganese oxides (MnO_x/Mn₃O₄) and reduced graphene oxide (rGO) are synthesized as active electrodes for energy storage devices. Comprehensive structural characterizations demonstrate that the active material is composed of MnO_x/Mn₃O₄ nanorods and nanoparticles embedded in rGO nanosheets. The development of such novel structures is facilitated by the extreme synthesis conditions (high temperatures and pressures) of the liquid-confined plasma plume present in the Laser Ablation Synthesis in Solution (LASiS) technique. Specifically, functional characterizations

demonstrate that the performance of the active layer is highly correlated with the $\text{MnO}_x/\text{Mn}_3\text{O}_4$ to rGO ratio and the morphology of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ nanostructures in HNCs. To that end, active layer inks comprising HNC samples prepared under optimal laser ablation time windows, when interfaced with a percolated conductive network of electronic grade Graphene and carbon nanofibers (CNFs) mixture, indicate superior supercapacitance for functional electrodes fabricated *via* sequential inkjet printing of the substrate, current collector layer, active material layer, and gel polymer electrolyte layer. Electrochemical characterizations unequivocally reveal that the electrode with the LASiS synthesized $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO composite exhibits significantly higher specific capacitance compared to the ones produced with commercially available Mn_3O_4 -Graphene NCs. Moreover, the galvanostatic charge-discharge (GCD) experiments with the LASiS synthesized HNCs show a significantly larger charge storage capacity (325 F/g) in comparison to NCs synthesized with commercially available Mn_3O_4 -Graphene (189 F/g). Overall, this study has paved the way for using LASiS-based synthesized functional material in combination with additive manufacturing techniques for all-printed electronics with superior performance.

2.1 Introduction

The increased global need for renewable energy technologies has inspired much research including development of next generation electrochemical energy storage devices such as supercapacitors (SCs) [68, 90]. However, many challenges including durability, cost, and environmental impact have to be addressed before these technologies are adopted on the global scale. SCs, either double-layer (EDLCs) and/or Faradaic (pseudocapacitors), are an attractive alternative to typical batteries due to their higher power density and longer life cycles. Specifically, SCs have a much higher energy density than conventional capacitors and can undergo multiple charge/discharge cycles at ultra-fast rates. They also offer higher power density and extended lifetime compared to conventional batteries. However, their charge storage capacity is typically much lower than batteries [109], partly due to utilization of carbonaceous material-based electrodes with an inherent lower energy density [138]. Hence, despite the aforementioned advantages of SCs, SC-based energy storage devices are

still not widely utilized as an alternative to traditional energy storage systems [42]. To that end, in recent years utilization of green electrochemical active materials with high specific capacitance, namely, transition metal oxides, *e.g.*, MnO, RuO, NiO, and Co₃O₄ has attracted much attention. However, this class of material lack many desirable properties of carbonaceous materials, including high specific surface area, high electrical and thermal conductivity, chemical stability, and low cost [54]. Consequently, more recent studies have been mainly focused on novel synthesis routes to develop nanostructured hybrid materials composed of transition metal oxide and various nanostructures of carbon to exploit their synergistic effects in electrochemical energy storage devices [54].

In addition to the aforementioned limitations of current SCs, the areal capacitance of SCs is limited due to the low material loading per unit area on the substrate. Increasing the thickness of the electrode is not a viable solution to this problem as the capacitance significantly decreases due to the sluggish ion diffusion in the bulk structure. To that end, three-dimensional (3D) electrodes with a high aspect ratio provide much promise [93]. Although the present energy storage manufacturing technologies can be used to produce the main components of SCs, namely, electrode, electrolyte, current collector, and device assembly, many challenges including optimal electrode configuration and economic consideration for large scale adaptation of this technology remain at large [? 125]. Amongst existing technologies, 3D printing is an alternative for the manufacturing energy storage devices [4]. Accordingly, the fabrication of SCs *via* sequential printing provides a synergistic advantage that brings the excellent durability and longevity of SCs with the precision and efficiency of 3D printing techniques [35]. To that end, additive manufacturing (AM) has been adopted to produce SCs *via* sequential printing of individual layers [36]. Specifically, inkjet printing provides the precision and low cost required for mass production of SCs with improved energy and power densities [14, 13].

Graphene and reduced Graphene oxide (rGO) inks have emerged as carbonaceous material of choice for printing electronics devices *via* inkjet printing[72]. Although GO and rGO have exceptionally large specific surface area, good chemical and thermal stability, and high electrical and thermal conductivity, their low energy density limits their utility as electrodes with high supercapacitance [75]. In general, electrodes composed solely of such

materials fail to meet the energy density desired for most practical applications. However, combination of transition metal oxides, namely, manganese oxide (Mn-oxide) species known for its high specific capacitance with Graphene/rGO has been successfully used in an array of applications, including sensors [78], and supercapacitors[71]. It should be noted that much attention has been focused on Mn-oxide as it is well-known for its unique and highly diverse valence and oxidation states (up to VII) of Mn, along with its rich redox chemistry. To that end, diverse classes of Mn-oxides are highly promising candidates for electrode materials in supercapacitors. However, most if not all the state-of-the art chemical synthesis routes currently used to produce high-quality Mn-oxide/rGO-interfaced HNCs are costly and complex. [31].

Our group has previously developed and patented the Laser Ablation Synthesis in Solution-Galvanic Replacement Reaction (LASiS-GRR) technique [88, 89] for the synthesis of diverse classes of intermetallic nanoalloys [51] and nanocomposites as electrocatalysts [52], and have specifically, adopted LASiS-based techniques for the synthesis of Metal Oxides (MO_x), Metal Organic frameworks (MOFs)[103], and MOF-derived HNCs [104]. The current study aims to introduce a simple, rapid, and inexpensive method to fabricate reduced Graphene oxide interfaced with nanostructured manganese-based metal oxides *via* LASiS and evaluate their application as advanced electrodes for supercapacitors. To that end, $\text{MnO}_x/\text{Mn}_3\text{O}_4$ has been selected as the metal oxide components for the HNC, owing to its well-known theoretically high specific capacitance and widespread use as electrodes in supercapacitor device. Specifically, herein, we demonstrate that selective tuning of the functionality of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs by tailoring their structure-property relations *via* LASiS-driven routes enable rational design and fabrication of efficient SC electrodes using metal-oxide/carbon-based HNCs. In addition, we also demonstrate the successful integration of optimally synthesized HNCs with suitable solvents, viscosity modifiers, commercial Graphene, and binders to prepare active layer inks for the fabrication of sequential inkjet printed supercapacitors with exceptional properties. Overall, this study has paved the way for use of LASiS-based synthesized functional material in combination with standard AM techniques for the fabrication of printed electronics with superior performance.

2.2 Synthesis of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs *via* LASiS-GRR

All chemicals and supplies used in this study were purchased from Sigma-Aldrich. GO was prepared from graphite flakes through one-pot synthesis by the improved Hummer's method [81]. Manganese (Mn) pellets (99.95% pure, 1" diameter in 0.125" thickness), were purchased from Kurt J. Lesker company. The LASiS-driven synthesis technique employed here is identical to what has been described in detail and reported in our previous studies. [54, 53, 103, 104] Specifically, the in-house prepared solution of GO suspensions in deionized water, with a concentration of 20 mg/L, was bath sonicated for approximately 60 minutes and then, transferred to the LASiS reactor cell. The Mn pallet was mounted on a holder at the bottom of the reactor cell and ablated using a pulsed Nd-YAG Laser (1064 nm) with 168 mJ/pulse energy at 10 Hz repetition rates for specific time windows between 6-10 minutes. The final product was in turn decanted for 24 hrs using deionized water and collected after the suspension was centrifuged at 4700 rpm for 22 minutes.

Post-treatments: To synthesize $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs, the final product was vacuum dried for 24 hrs followed by vacuum heating at 250 °C for 3 hrs.

The entire HNCs synthesis process is schematically depicted in Figure 2.1

2.3 All-printed supercapacitor: Methods and materials

The advantages of the 3D printed SCs in this study include rapid prototyping of 3D electrode architectures and improved device performance. High porosity and large specific surface area are other significant benefits of 3D-printed electrodes, which not only can improve the contact area between electrodes and electrolyte but also can increase the electrochemical performance. Furthermore, as reported in the current study, manufacturing the entire device *via* a 3D printing technique reduces the cost and complexity of the manufacturing facility while increasing versatility and production capacity.

In our design, conductive silver (Ag) nanoparticle pastes with the resistivity of $1.59 \mu\Omega\cdot\text{cm}$ at 20°C serves as the current collector layer of the printed design schematically shown in Figure 2.2; the Ag layer was printed and annealed at 120°C for 1 hr. The active layer of the Faradaic SC is composed of Mn-oxide/carbon-based electroactive materials interfaced with electronic grade Graphene nanoflakes from IG LLC and, carbon nanofibers (CNFs), ethyl-cellulose (E-C) and terpineol from Sigma-Aldrich. The electroactive components comprise either a commercial-grade Mn_3O_4 -Graphene nanocomposites (NCs) (99.5% purity, Mn_3O_4 :Graphene = 1:1) obtained from US Research Nanomaterials Inc., or an in-house LASiS-derived $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGo HNCs to allow direct comparison of their respective supercapacitive performance. Specifically, to ensure effective charge transport *via* a percolated conductive network, Graphene nanoflakes (0.9 g) and CNFs (0.1 g) are added to both the commercial Mn_3O_4 -Graphene NCs and LASiS-made $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs (0.2 g). In turn, the respective active layers were dispersed in 45 mL of methanol. The solution was bath-sonicated for 1 hr followed by evaporation of methanol at 40°C under vacuum conditions for approximately 12 hrs. The resulting powder was dispersed in 3 mL of terpineol by manual stirring. Finally, 0.5 g of E-C was added to the powder and terpinol solution by manual stirring for several minutes. The gel polymer electrolyte (GPE) layer was prepared by dissolving polyvinylidene difluoride (PVDF) and lithium perchlorate (LiClO_4 , 0.25 M) as the salt (PVDF: LiClO_4 = 2:1) in propylene carbonate at 140°C with continuous stirring for 1 hr. After the GPE layer solution turned into a viscous gel upon cooling, it was printed on the active layer.

The device patterns were assembled by sequential 3D printing procedure (one layer at a time) shown schematically in Figure 2.2(a). Printing patterns for the active and current collector layers were initially developed in Solidworks software (2018, Dassault Systèmes SolidWorks Corp., MA, USA). Interdigitated patterns of the current collector and active layer comprise eight lines in total (size and dimensions are discussed in Figure 2.9. and 2.11), four lines for the positive and four for the negative electrode (Figure 2.2(b)). Evidently, the size and shape of the pattern can be customized depending on the system requirements. After trying various printed designs on different substrates, the fillet pattern in Figure 2.2(b) was selected for a combination of reasons, namely, simplicity, printer compatibility, and

reproducibility. Upon investigation of the printing results on various substrates, acrylonitrile butadiene styrene (ABS) was selected as the substrate. The substrate was printed using filament printing methods with a large format fused deposition (FD) printer (Model: Raise3D Pro2 3D Printer (Figure 2.10)) by heating the printing nozzle to the specific temperature required for printing of ABS filament, namely, 240°C. It should be noted that printing of ABS filament requires nozzle temperature of 210 - 250°C, as well as a heated bed with a temperature range of 80 to 110°C. Furthermore, ABS needed to be printed in an enclosed print chamber and cooled down slowly to avoid any possible shrinkage and/or warping. [100] The reason to utilize our custom 3D printed substrates is to maximize the benefits of an all-printed device fabrication process and to avoid the challenges in implementation of prefabricated substrates as illustrated in Figure 2.11. After printing the ABS substrate, the substrate was kept at room temperature for 10 minutes to allow solidification. Later, the substrate was rinsed with methanol and propylene to remove all possible contamination. The surface roughness of the printed substrate was maintained to facilitate ink adhesion (Figure 2.11).

In turn, sequential layer-on-layer printing was used to assemble the final all-printed SC design (Figure 2.2(c)). The current-collector, active layer, and the GPE layer were printed by the Engine HR printer (Model: Hydra 16A printer of Hyrel 3D EHR system). The silver (Ag) paste was printed on the substrate as a current collector layer using an inkjet printer based on the pattern designed on Solidworks software and was annealed at 120°C for 1 hr. Due to its high conductivity, the Ag current-collector facilitates a rapid charge transfer from the active layer. The active layer of the SC is intended to provide a fast surface redox reaction in the printed system. It should be noted that the viscosity, cure temperatures, software parameters, and $\text{MnO}_x/\text{Mn}_3\text{O}_4$ particle sizes were tailored to allow optimal printed designs and prevent printing failures such as shortcuts between electrodes due to "oozing" of the ink. The active layer is printed on the Ag layer and then subjected to a thermal treatment at 80°C for 1 hr. Specifically, the active layer was prepared by dispersing the desired HNCs in the previously prepared paste composed of Graphene, CNFs, and E-C. Finally, The GPE layer was printed on the top of the active layer and dried at room temperature overnight. The

aforesaid process was identically repeated for fabricating the control electrodes comprised of commercial Mn_3O_4 -Graphene NCs for a comparison of SC performances.

Structural, compositional, and morphological characterization

The HNCs were first characterized by: (1) X-ray diffraction (XRD) analysis with a Phillips X'Pert-Pro diffractometer with a $\text{Cu K}\alpha$ monochromatized radiation source ($\lambda = 0.1541\text{nm}$) operating at 45 kV, and 40 mA, (2) Philips XL-30ESEM scanning electron microscope equipped with energy-dispersive X-ray (EDX) spectroscopy, (3) Nicolet iS50 FT-IR Spectrometer, and (4) Helios 5UX dual beam FIB/SEM.

2.4 Electrochemical characterization

A conventional, three-compartment electrochemical (EC) cell from Pine Instruments, LLC containing a saturated double junction Ag/AgCl reference electrode and a Pt counter electrode was utilized for all EC characterizations of the HNCs. All EC characterizations were carried out with a three electrode configuration for the ink prepared from the Laser-based HNCs and with a two-electrode configuration directly on the electrodes of the printed device. Specifically, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) experiments were performed using a research-grade potentiostat (SP-150, Biologic instrument).

2.4.1 Supercapacitance measurements: LAsiS-based $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs

An in-house working electrode was fabricated for the electrochemical supercapacitance properties of all HNCs. Initially, a slurry mixture was prepared by vigorously stirring a mixture of 80% of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs, 10% of acetylene black (Cabot), and 10% of polyvinylidene difluoride (PVDF, Aldrich) binder. Thereafter, $\sim 3\text{-}5\text{mg}$ of the resulting slurry was drop-cast on a highly porous squared-shape Nickel (Ni) foam (1cm^2). The loaded Ni foam substrate was then dried under vacuum at 80°C for 8 hrs, and subsequently pressed at 10 MPa for 5 seconds. 0.5 M Na_2SO_4 (pH 7.2) is used as the supporting electrolyte to

improve the electrolyte conductivity. Cyclic voltammetry (CV) tests were performed in a fixed potential range of -0.50 to 0.30 V at a scan rate of 20mV/s. The cyclic charge-discharge (CD) tests were evaluated at a current density of 2A/g over a potential range from -0.50 - 0.30 V. The capacitance is in turn calculated from the CD curves as follows:

$$C = \frac{I_m \times \Delta t}{\Delta V} (Fg^{-1}) \quad (2.1)$$

where $C(F/g)$ is the specific capacitance, $I_m = \frac{I}{m}$ (A/g) is the current density (current per unit mass) during discharge, $m(g)$ is the weight loading of the electroactive material, and $\Delta V(V)$ is the potential drop.

2.4.2 Supercapacitance measurements for the printed SC device

CV tests were performed in the potential range of 0.0 to 0.80 V at a scan rate of 20mV/s. The cyclic charge-discharge (CD) tests were evaluated at a current density of 1A/g over a potential range from 0.0 to 0.80 V. The capacitance is in turn calculated from the CD curves, where the capacitance value is obtained by multiplying the capacitance relation depicted in Eq. 1 by a factor of 2, owing to the series of capacitance formed in two electrode system.

2.4.3 Characterization of all-printed SCs

Thermogravimetric analysis (TGA) was performed on a standard TA Instrument (Q50 15GA) by heating the samples at a rate of 10°C/min from ambient temperature to 600°C and 800°C in an inert N₂ environment to ascertain the thermal properties and stability of the Laser-derived (MnO_x/Mn₃O₄-rGO)/commercial (Mn₃O₄-Graphene) HNCs, ink, binder, and solvent. In addition, the data is used to estimate the wt% of the electroactive component.

2.5 LASiS synthesized $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs

2.5.1 Structural and morphological characterizations

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to examine the structural and morphological characteristics of the LASiS-synthesized HNCs. The direct comparison between XRD pattern of the sample prepared under 8 minute of ablation time and the sample containing the standard commercial Mn_3O_4 -Graphene NCs show the emergence of unique and dominant crystalline structures in the LASiS-synthesized nanomaterials (Figure 2.3(a)). XRD peak patterns indicate that various oxide structures, namely, MnO , MnO_2 and Mn_3O_4 , are likely present in the composite $\text{MnO}_x/\text{Mn}_3\text{O}_4$ nanostructures formed during the LASiS-induced synthesis of the HNCs subjected to post-synthesis heat treatments. Comparison of the standard XRD patterns for $\text{MnO}/\text{MnO}_2/\text{Mn}_3\text{O}_4$ and the XRD patterns collected for the as-synthesized $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs indicate considerable presence of crystalline MnO (face-centered cubic) and MnO_2 (Hollandite; α - MnO_2) structures along with a significant amount of Mn_3O_4 (tetragonal and orthorhombic) structures. Specifically, the mass ratio (wt%) of $\text{MnO}:\text{MnO}_2:\text{Mn}_3\text{O}_4$ is calculated to be 28:8.7:63 in the sample prepared under 8 minutes of ablation time. In the case of the commercial HNC, only clear diffraction patterns of crystalline Mn_3O_4 are observed. On the other hand, XRD patterns of samples prepared under 9- and 10- minutes of ablation times indicate negligible presence of MnO_2 crystal structures in the HNCs (see Figure 2.15). The wt% of the different Mn-oxide crystalline structures present in the composite $\text{MnO}_x/\text{Mn}_3\text{O}_4$ samples prepared with different ablation time is summarized in Table 1. In addition, Fig3(b) depicts the FT-IR spectra of pure Mn_3O_4 and $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO samples prepared with 8 minutes ablation time. Hereon, the vibration bands around 595, 445 and 481 cm^{-1} are attributed to the stretching of the Mn-O bonds in Mn_3O_4 NPs and $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs [70, 61]. The presence of the Mn-O stretching vibration on the HNCs suggests the successful integration of the $\text{MnO}_x/\text{Mn}_3\text{O}_4$ with the rGO. These FT-IR results also advocate that the $\text{MnO}_x/\text{Mn}_3\text{O}_4$ nanostructured materials are embedded within the rGo nanosheets. In addition, results are also in full agreement with the SEM (Figure 2.4) and XRD data (Figure 2.3(a)) further highlighting the formation of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs.

Correspondingly, SEM micrographs of HNCs synthesized under different ablation times (6-10 minutes) are shown in Figure 2.4. The figure depicts uniformly grafted MnO_x nanorods (NRs) and trace amounts of spherical nanoparticles (NPs) on the rGO nanosheets. It also shows that the sample synthesized under 8 minutes ablation time has higher number densities of more well-dispersed NRs in the ensuing products. The NRs observed in SEM images can be attributed to MnO_2 and/or Mn_3O_4 structures based on XRD patterns, whereas the spherical particles are primarily MnO NPs.

Formation of the observed $\text{MnO}_x/\text{Mn}_3\text{O}_4$ NRs can originate from the nucleation of the "tunnel-like" $\alpha\text{-MnO}_2$ polymorphic structures from the LASiS-induced plasma dynamics. Such structures comprised of the characteristic corner-shared $[\text{MnO}_6]$ octahedral arrangements are known to be stabilized at nanoscale dimensions and have been reported to emerge in typical hydrothermal synthesis routes [127, 38, 128, 124]. Hence, it can be posited that these $\alpha\text{-MnO}_2$ crystallites can in turn undergo edge-to-edge growth resulting in tunnel-like structures that form the 1D NRs through solution-phase reactions. To that end, SEM images (Figure 2.4) together with XRD patterns (Figure 2.3(a) and Figure 2.13), support the observation of the $\alpha\text{-MnO}_2$ crystal structures (referenced to the standard XRD patterns for $\alpha\text{-MnO}_2$ in Figure 2.3(a)) and the formation of nanorods in the 8 minute ablation during the LASiS process. Specifically, the incipient $\alpha\text{-MnO}_2$ rod-shaped seeding sites can subsequently serve as the template for the growth of the Mn-rich phases. These Mn-rich species in turn experience Faradaic reactions, resulting in a mixed oxide composition, namely, MnO, MnO_2 and Mn_3O_4 stabilized at the nanoscale dimension. Herein, it is noted that the extent of conversion of Mn-rich phases in the incipient $\alpha\text{-MnO}_2$ structures into Mn_3O_4 phases *via* Faradaic reactions depend on the available initial concentrations of the $\alpha\text{-MnO}_2$ phase from the LASiS process. Hence the resultant MnO_2 concentrations (wt%) are different in the samples prepared under different ablation times (see Table 1). To that end, the aforesaid structural analyses from XRD measurements (Figure 2.3(a) and Figure 2.14) coupled with observations from the SEM micrographs (Figure 2.4) strongly suggest that the interplay between the specific wt% balance of the 3 manganese oxide phases (MnO, Mn_3O_4 and MnO_2) formed during the high-energy laser ablation processes plays a critical role in the capacitance behavior of the samples prepared under different ablation times. Hence, significantly higher

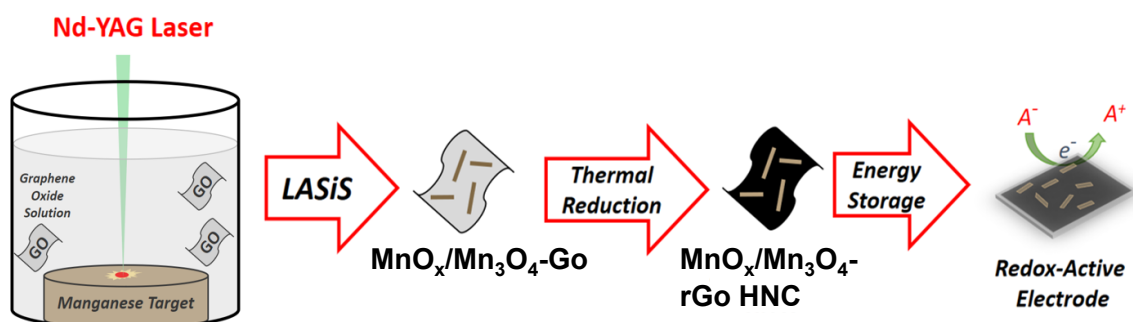


Figure 2.1: LASiS-based HNCs of nanostructured $\text{MnO}_x/\text{Mn}_3\text{O}_4$ interfaced with rGO with enhanced supercapacitive properties.

Table 2.1: The wt% of different manganese oxides in samples prepared with 8, 9, and 10-minute ablation time.

Samples	Mn_3O_4	MnO_2	MnO
8min	$63 \pm (1)$	$8.7 \pm (3)$	$28 \pm (1)$
9min	$69 \pm (2)$	*Negligible	$31 \pm (1)$
10min	$76 \pm (2)$	*Negligible	$23 \pm (1)$

*Below the limit of detection

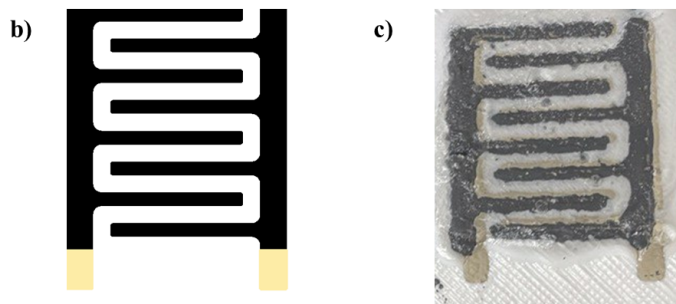
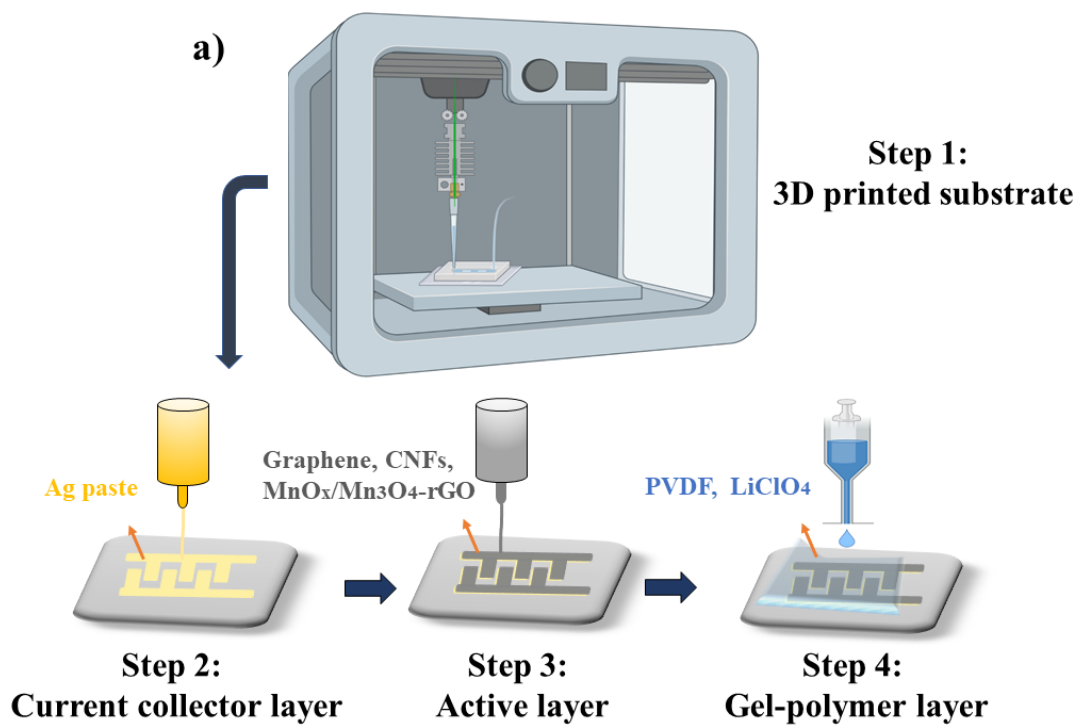


Figure 2.2: (a) Schematic illustration of the sequential layer-on-layer procedure for the 3D printing of SC electrodes; (b) Software generated interdigitated patterns for the current collector and active layers, (c) Final all-printed SC electrode design composed of printed substrate, current collector, active, and the GPE layers.

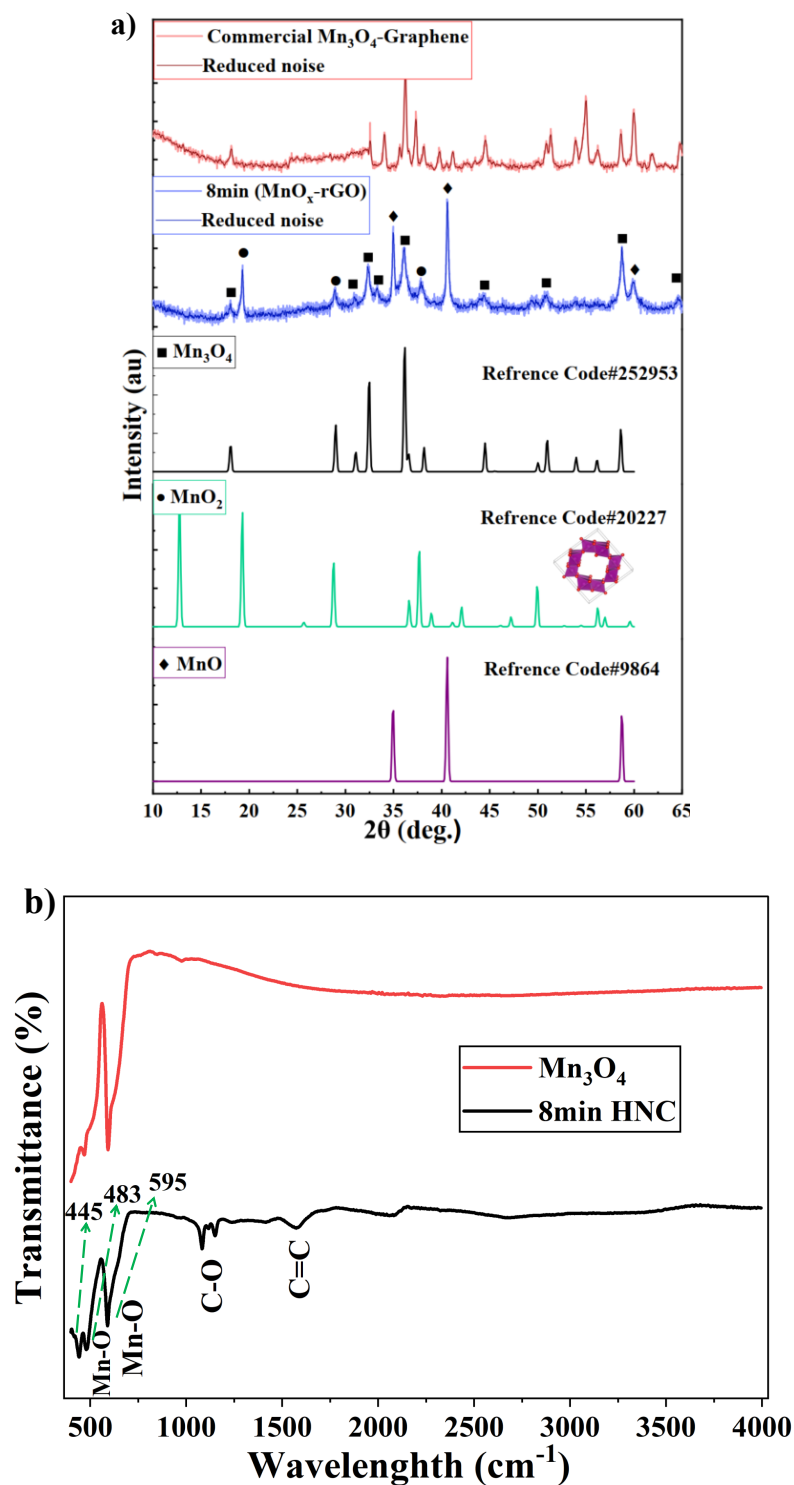


Figure 2.3: (a) XRD patterns for commercial Mn₃O₄-Graphene NCs and MnO_x/Mn₃O₄-rGO HNCs prepared under 8 minute ablation time along with the standard peak patterns for crystalline MnO, MnO₂ and Mn₃O₄ structures. (b) FT-IR spectrum of Mn₃O₄ (red) and synthesized HNCs (MnO_x/Mn₃O₄-rGO) under 8 min ablation time (black).

amount of MnO_2 (~ 8.7 wt%) in the NRs typically formed under 8 minutes of ablation time (see Table 1) can be ascribed to the aforementioned structure-morphology evolution promoted by the specific laser-induced plasma dynamics at the solution interface. The formation of this significant amount of MnO_2 in the 8-minute ablation samples will be shown to be critical in explaining the enhanced supercapacitance of the HNCs when inked onto the electrodes.

2.6 Functional characterizations

In this section, we present CV measurements [18] carried out at a scan rate of 20 mV/s for the scanning potential range of -0.50 to 0.30 V to provide qualitative analyses of the capacitive behaviors of the LASiS-synthesized $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs. To that end, Figure 2.5(a) shows the CV curves collected in Na_2SO_4 electrolytes for the various $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs prepared under different ablation time (6-10 minutes). It can be concluded from the enclosed area of the CV curves that the effective capacitance values show marked increase for the samples prepared under 7-9 minutes ablation times when compared to those collected from 6- and 10- minutes ablation times, with the maximum capacitive property occurring at 8 minutes. To further support these observations, direct quantitative analyses from discharge curves obtained at 2A/g from GCD electrochemical measurements (Figure 2.5(b)) clearly demonstrate longer discharge duration (~ 87 -180 minutes) for the HNCs prepared under 7-9-minute ablation times with the peak discharge time corresponding to the 8-minute ablation time. In contrast, drastic reduction in discharge times (< 40 minutes) is observed for HNCs synthesized under 6, and above 10 minutes of laser ablation. Finally, using Eq.(1), the specific capacitance values calculated from the GCD discharge curves for the HNC samples synthesized under different ablation times (6-10 minutes) are shown in Figure 2.5(c). It is noted that a maximum capacitance value of ~ 442 F/g is recorded for the $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs synthesized with 8 minutes of laser ablation.

A significant insight from the aforesaid results is the critical role of ablation times during LASiS in tailoring the relative volume loading, composition (wt% distribution of MnO , MnO_2 , Mn_3O_4) and structure of the as-synthesized $\text{MnO}_x/\text{Mn}_3\text{O}_4$ NRs in the rGO

matrix which, in turn, tunes the capacitive properties of synthesized HNCs by altering their ion diffusion pathways, conductivity and ultimately, charge transport properties. To that end, a higher density of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ NRs allows more charges to be stored due to the increased rate of Faradaic reactions with the electrolyte as a result of the increased interfacial area for electrolyte interactions. These observations need to be considered in conjunction with the fact that, at a critical concentration, redox reaction pathways can be stymied due to compromised charge transfer processes through the NCs due to the relatively low conductive nature of the oxide species. Therefore, the conductive nature stemming from the existence of rGO is crucial for enhancing the supercapacitive properties of MnO_x -rGO HNCs. The rapid charge transfer in the conductive sp^2 carbon network delivered by the rGO nanosheets suppresses charge accumulation on the $\text{MnO}_x/\text{Mn}_3\text{O}_4$ nanostructured surfaces, thereby enhancing the electrode/electrolyte interfacial charge transport and higher power outputs. Furthermore, the distinctly enhanced supercapacitive and discharge curve behaviors shown above (see Figure 2.5(a) & (b)) for the HNCs synthesized under 7-9 minute ablation times (with the best SC performance from the 8-minute ablation sample) can be directly correlated to the emergence of a significantly higher number of well-dispersed $\text{MnO}_x/\text{Mn}_3\text{O}_4$ NRs (seen from Figure 2.4) and the significantly higher amount (wt%) of MnO_2 present in the 8 minute ablation sample (see Table 2.1). Hence, it can be posited that the excess interfacial areas and tubular channel-like pathways for the NRs comprised of higher α - MnO_2 contents, that emerges from the high-energy LASiS-induced processes, play a significant role in promoting superior charge transport and fast ion diffusion properties. It would be worth highlighting that previous studies have conclusively established that the tubular structures of the α - MnO_2 phase make them promising candidates as SC electrode materials. This can be attributed to their optimal tunnel spaces that can essentially control the electrolyte ion adsorption rates on the crystalline MnO_2 structures on inner tunnel surfaces which, in turn, has an immediate impact on the charge storage process during the redox reactions. [132, 27, 16, 116].

As mentioned before, charge transfer mechanisms and Faradaic reaction rates are both essential elements in optimizing the supercapacitive properties of Mn oxide-rGO HNCs. Hence, we have investigated the optimal ratio of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ NRs to the carbonaceous

rGO matrices *via* TGA experiments on the as-synthesized HNC samples. Figure 7(a) depicts the thermal properties of LASiS-derived HNCs and commercial NCs at a scan rate of 10°C up to 800°C under N₂ atmosphere. The Mn₃O₄-Graphene and MnO_x/Mn₃O₄-rGO plots show a two-step thermal degradation process with about 26 and 24.8 wt% initial weight loss up to around 550°C, respectively. The removal of adsorbed water/moisture and elimination of some residual oxygen containing elements from GO could be attributed to the initial weight loss of commercial and laser derived HNCs up to 220°C. The sharp weight loss at higher temperatures (between 350-500°C) may be ascribed to the decomposition of the oxygen containing functional groups present in the GO sheets and successful reduction process of GO. Finally above 550°C, the residue weight percentage of manganese oxide in the Mn₃O₄-Graphene NCs and MnO_x/Mn₃O₄-rGO HNCs is 74 and 75.2 wt%, respectively which is mainly ascribed to the higher residual metal oxides mass present in the LASiS synthesized HNCs at 800°C. Thus, the aforesaid TGA analyses for Mn-oxide: rGO compositional ratios can be directly correlated to the effective supercapacitive properties seen in Figure 2.5 and the SEM images in Figure 2.3(a). Specifically, a clear symbiotic Faradaic and conductive relation is required for superior capacitive properties. Hence, Faradaic properties of MnO_x/Mn₃O₄-rGO HNCs that arise from Mn oxide and rGO is crucial to the conductivity of the electrode material.

2.6.1 Printed Supercapacitor

Properties of the Printed Layers

SEM micrograph images in Figure 2.6 illustrate the structure of the as-printed active SC layer before (Figure 2.6(a)) and after (Figure 2.6(b)) the addition of E-C binder and the heat treatment steps. For comparison purposes, Figure 2.14 depicts the SEM micrographs of each of the active-printed electrode constituents in their respective pristine phases. On the other hand, Figure 2.16 depicts the EDS spectra of MnO_x/Mn₃O₄-rGO HNCs on a Si wafer. Taken together, these figures clearly confirm the presence of Mn, C, and O components. Specifically, Figure 2.6(a) clearly shows a percolated network formed by the combination of long CNFs (1D) and electronic grade Graphene nanoflakes (2D) interfaced with the active

MnO_x/Mn₃O₄-rGO HNCs. Herein, the presence of the space filling 2D Graphene nanosheets promote the effective immobilization of the MnO_x/Mn₃O₄ NRs/rGO HNCs on their surfaces while the micron-sized CNFs provide the much-needed 1D conductive paths for efficient charge transfer between the Graphene nanoflakes (see Figure 2.13 and 2.14. In fact, the ability of the nanostructured metal oxide (MnO_x/Mn₃O₄) phases to enhance the overall capacitance of the supercapacitor cell is ascribed to a series of electrochemical lithiation reactions originating at the LiClO₄-based GPE layer, outlined in detail in Figure 2.10-2.13. Specifically, the flux of charges arising from the above-mentioned redox reactions occurring at the nanostructured metal-oxide/gel-polymer electrolyte interface is rapidly transferred to the rGO basal plane and, subsequently, to the Graphene nanoflakes, which then conducts these charges through the percolated conductive CNF paths, ultimately transporting them to the current collectors.

For ease of visualization, the enlarged inset in Figure 2.6(a) indicates the color-coded MnO_x/Mn₃O₄ NRs and the rGO nanoflakes. Furthermore, the composition of the active SC components quantified *via* the wt% of CNFs, electronic grade Graphene nanoflakes and the electroactive MnO_x/Mn₃O₄-rGO HNCs, are shown in Table 2.2.

In order to investigate the thermal stability of the all-printed SC electrode layers after the 80°C annealing treatments (as described in the methodology section 2.5), subsequent TGA was also performed on the printed ink with the active materials in an N₂ environment. The TGA test results shown in Figure 2.7(b) are intended to establish the thermal stability of the MnO_x/Mn₃O₄-rGO content in the ink material and the HNCs structures. The initial large mass change of ~60 wt% in the SC ink denotes the evaporation of the organic solvent (terpineol) at an onset temperature of ~200°C. The second significant mass change of ~20 wt% occurs between 200 - 350°C that indicates the complete degradation of the binder. From 350°C forward, the solvents are completely evaporated, and the mass loss shows the thermal decomposition of the E-C in the binder. These results confirm that the processed active layer used in the printed SC ink after the annealing process is composed of ~20 wt% of the as-synthesized HNCs. Since there is no significant mass change in samples annealed at 100°C (Figure 2.7(b)), it can be concluded that the inks did not undergo any thermal decomposition during the annealing process.

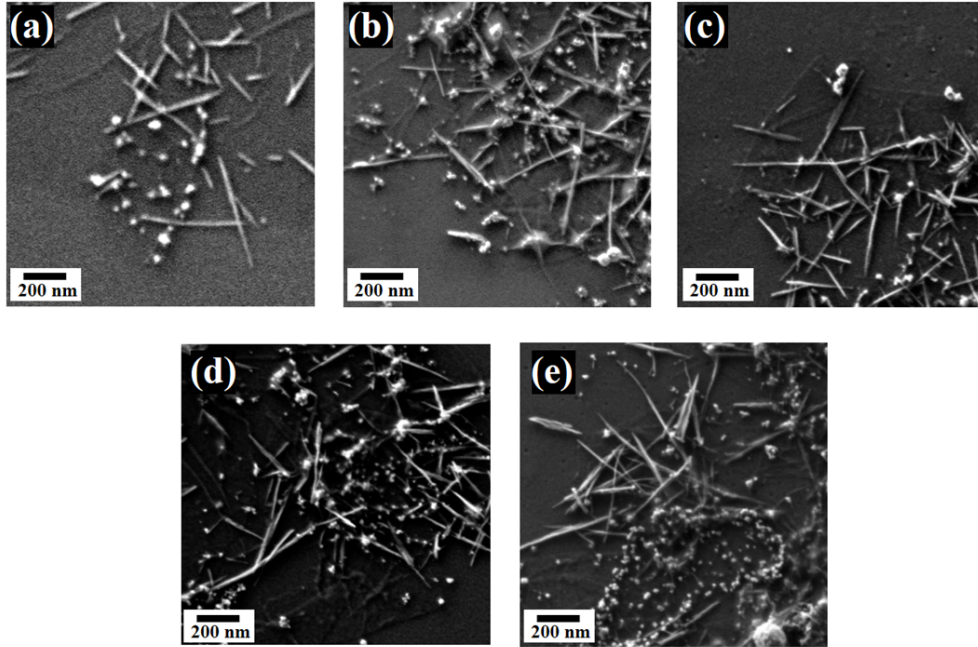


Figure 2.4: SEM micrographs of $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs prepared *via* LASiS under (a) 6 minute (b) 7 minute (c) 8 minute (d) 9 minute and (e) 10 minute ablation time.

Table 2.2: The wt% of CNF/Graphene matrix to laser derived ($\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO) HNCs in the prepared SC ink material.

SC ink Material	CNF	Graphene	Laserderived HNCs
weight percent(%)	9	75	16

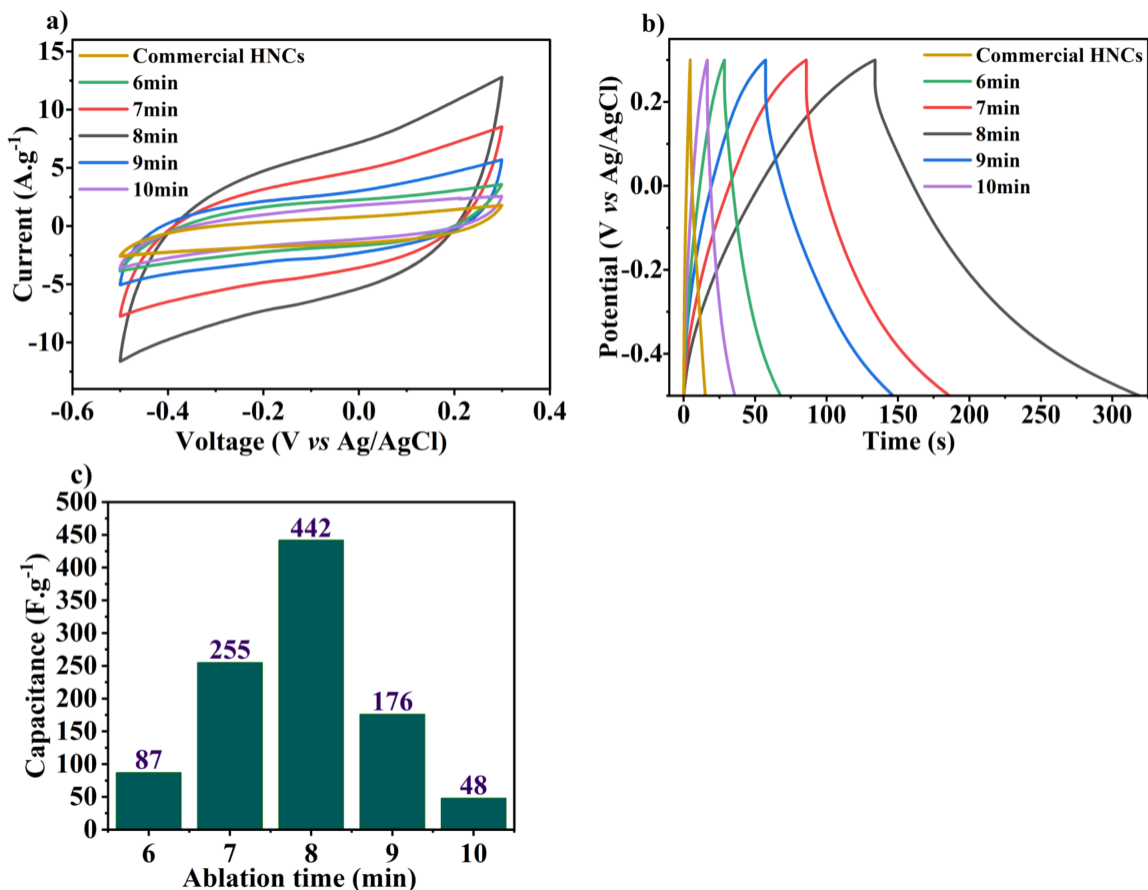


Figure 2.5: (a) CV curves in 0.5 M Na₂SO₄, and (b) discharge curves at 2 A/g for LASiS-synthesized MnO_x/Mn₃O₄-rGO and commercially-made HNCs; (c) calculated capacitance values (F/g) for MnO_x/Mn₃O₄-rGO HNCs synthesized under varying ablation times (6-10 minutes).

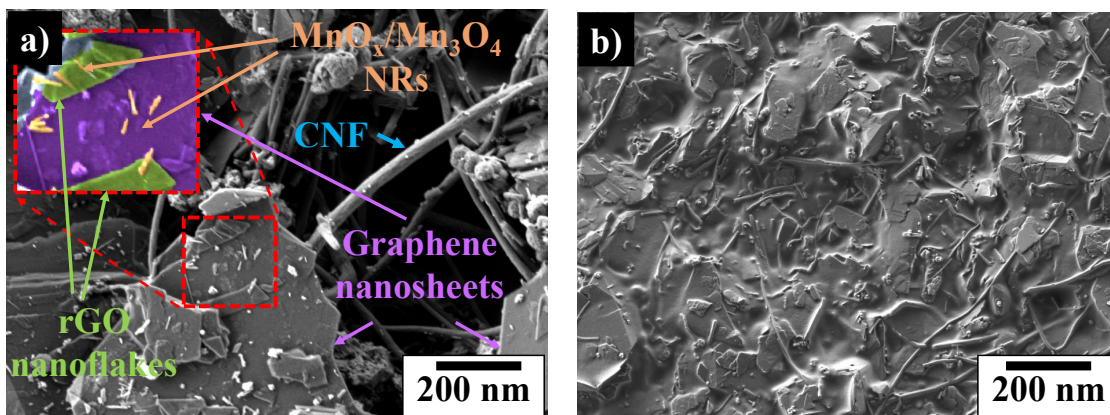


Figure 2.6: Structure of the SC ink material shown by the SEM images of (a) percolated networks of CNFs and MnO_x/Mn₃O₄ NRs on Graphene nanosheets before heat treatment, and (b) printed active layer containing E-C binder after heat treatment at 80°C.

2.7 Electrochemical Analysis of the Printed SCs

Finally, CV measurements are conducted on the all-printed SC electrodes over a potential range of 0.0 to 0.80V at a scan rate of 20 mV.s⁻¹ (Figure 2.8(a)). CV curves are indicative of the well-known potential scan profiles for material that exhibit capacitive behavior, namely, broadened current spread and absence of redox peaks. This indicates a proper pseudocapacitance performance with symmetrical redox behavior and fast reaction rates that arise from the active MnO_x/Mn₃O₄-rGO HNCs. The CV analyses clearly indicate that the capacitive properties increase for the printed SCs incorporating the LASiS-synthesized MnO_x/Mn₃O₄-rGO HNCs as the electroactive materials as compared to ones using the standard commercial HNCs. Moreover, the discharge curves in Figure 2.8(b) exhibit longer discharge times for the printed SC comprising LASiS-synthesized HNCs as compared to the SC comprising commercial-grade Mn₃O₄-Graphene NCs. The GCD characteristics with discharge currents of 1.0 A/g exhibit the same expected supercapacitor behavior (Figure 2.8(b)). The values of gravimetric capacitance (also called specific capacitance, C_{sp}) are calculated from the discharge characteristics. C_{sp} values for the SCs composed of LASiS-Synthesized and commercial HNCs materials at a current density of 1.0 A/g are 325 F/g and 189 F/g, respectively (Figure 2.8(b)).

The shape and size of the printed pattern can be customized and will be studied in the future works. In this study, fillet pattern was developed to handle the convenience, printer compatibility, and reproducibility while improving the strength of printed design by avoiding right angle and also keeping consistent printing (Figure 2.9). As can be seen in Figure 2.10, the role of the substrate is to support all other functional layers including current-collector, active, and Gel Polymer layers. As you see in this figure, the surface roughness of ABS printed substrate was maintained to help with the ink adhesion.

Examples of substrates failures:

As illustrated in Figure 2.11, the printing failures on the substrate were the main reason for using our custom 3D printed ABS substrate instead of these prefabricated commercially existing substrates to fabricate an all-printed SC design. The printed ABS substrate could support the current collector, active and gel polymer layer and it was perfectly compatible

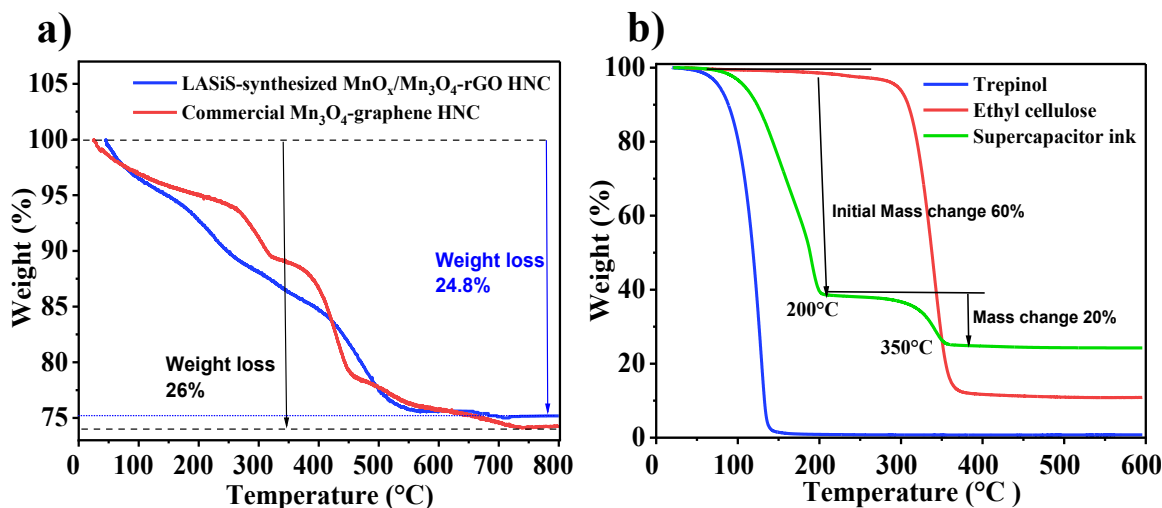


Figure 2.7: Physicochemical properties of the printed ink and HNCs analyzed *via* TGA of: (a) commercial (red) and LASiS-synthesized (blue) HNCs, and (b) printed ink (after vacuum drying of solvents), solvent, and binder.

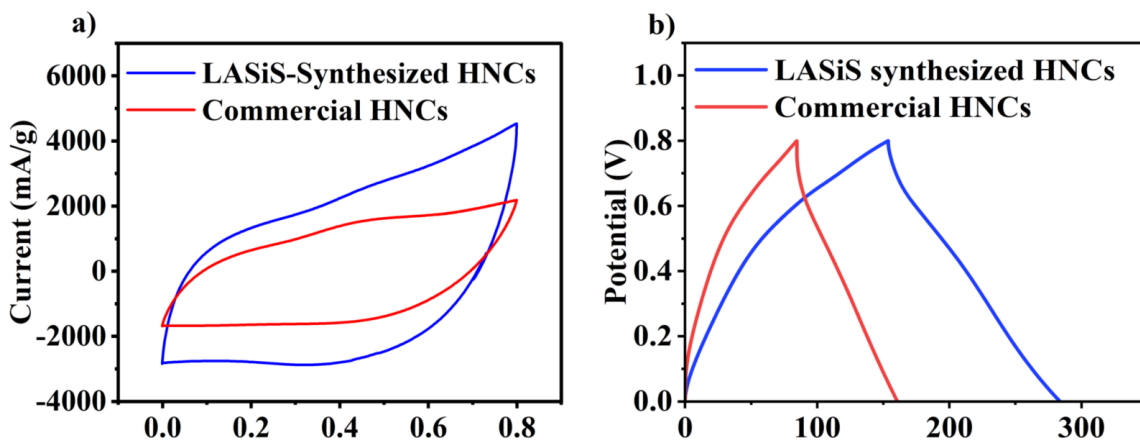


Figure 2.8: Electrochemical performances of all-printed SCs as recorded from: (a) CV curves at 20 mV/s scanning rate for the printed SCs containing commercial (red) and LASiS synthesized (blue) $\text{MnO}_x/\text{Mn}_3\text{O}_4$ -rGO HNCs and (b) discharge curves at 1 A/g.

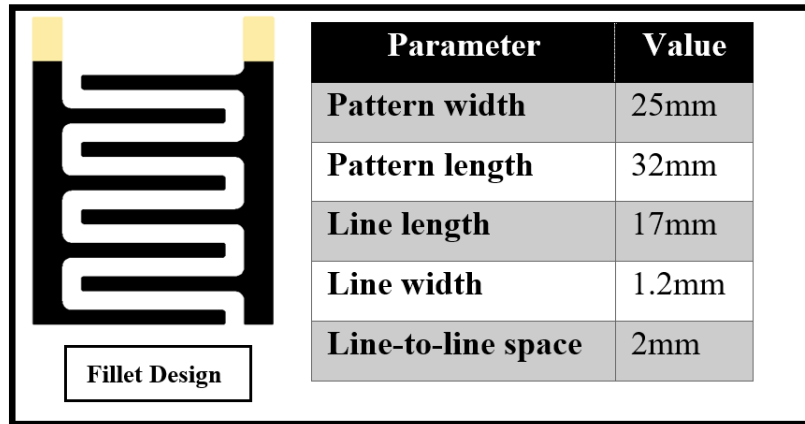


Figure 2.9: Interdigitated fillet printing pattern of the silver current collector, active layers, and printed design dimensions.

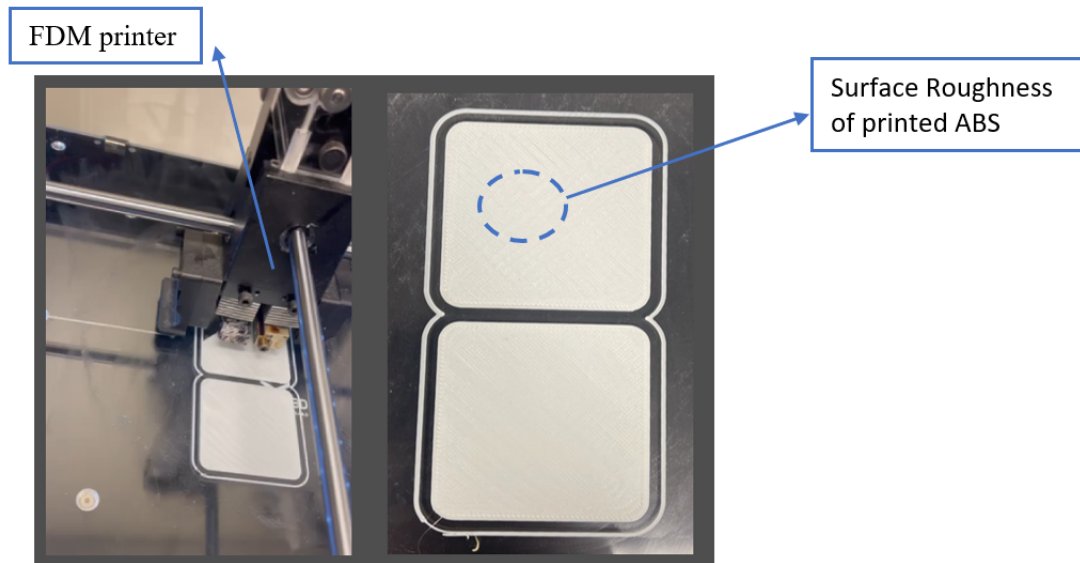


Figure 2.10: The filament printed ABS substrate fabricated by an FDM printer.

with the annealing temperature required for each layer. Therefore, no thermal degradation (cracking, chipping, and breaking) was observed. ABS did not show any adhesion failure and it was also compatible with the solvent we used to prepare the gel polymer layer.

From CV plot:

Specific capacitance (C_s) from CV

$$C = \frac{\int I_m dV}{V \Delta V} (F g^{-1}) \quad (2.2)$$

C_s (F) specific capacitance (The gravimetric capacitance (or specific capacitance, C_{sp}), $I_m \cdot dV$ integrated area under curve. m (g) mass of active material on electrode surface. ΔV (V) is the difference in potential window and V (mVs^{-1}) is the potential scan rate (ie 20 mV).

For synthesized Ink, printed SC

At $V = 20$ mV synthesized:

$$I_m \cdot dV = \text{Area}(cv \text{ plot}) = 5575.4$$

$$\Delta V = \text{Final-Initial} = 0.9 - (-0.1) = 1 \cdot 100 \text{ V}$$

$$C_s = 5575.4 / 20 \cdot 0.61 \cdot 1 = 278.8 \text{ F/g}$$

For Commercial Ink, printed SC

At $V = 20$ mV synthesized,

$$I_m \cdot dV = \text{Area}(cv \text{ plot}) = 4410.15$$

$$\Delta V = \text{Final-Initial} = 0.9 - (-0.1) = 1 \cdot 100 \text{ V}$$

$$C_s = 4410.15 / 20 \cdot 0.85 \cdot 1 = 187.7 \text{ F/g}$$

From GCD plot:

$$\Delta Q = \frac{C}{\Delta V}; C(\text{capacitance}) = \frac{\Delta Q}{\Delta V} \quad (2.3)$$

Specific capacitance (C_p) from GCD

$$C_p(\text{specific capacitance}) = \frac{\Delta Q}{m \Delta V} \quad (2.4)$$

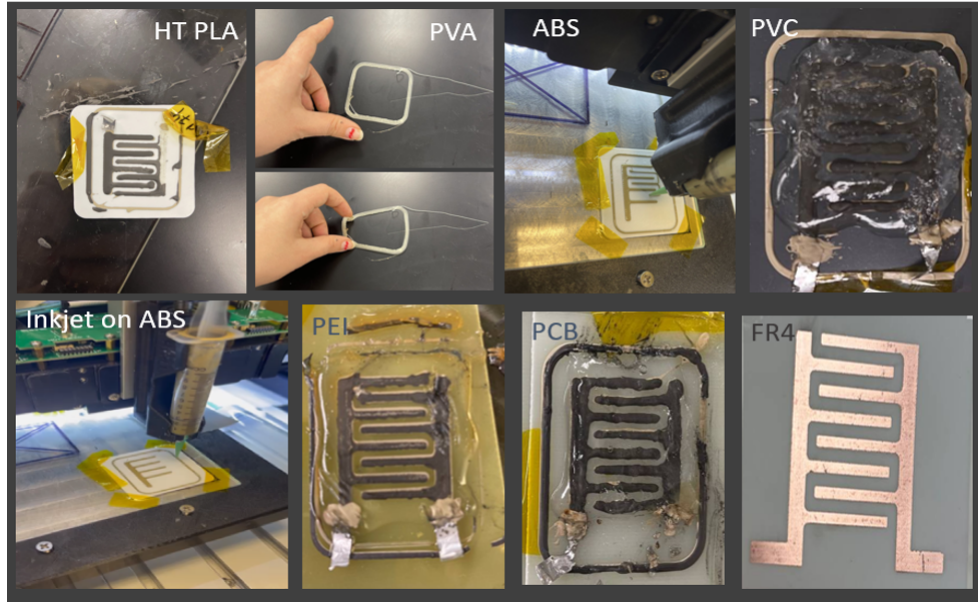


Figure 2.11: Various prefabricated substrates were investigated in this study (such as, Polyvinyl alcohol (PVA), High Temperature Polylactide (HTPLA), Polyvinyl chloride (PVC), Polyetherimide (PEI), etc.).

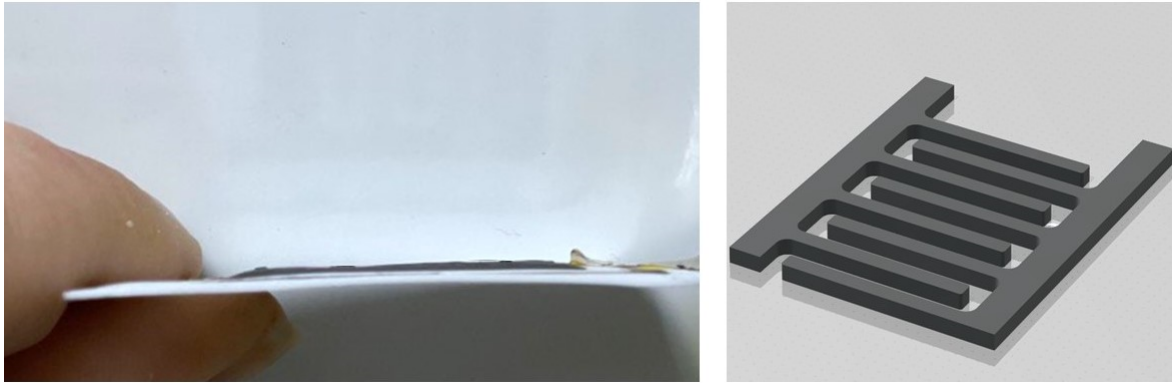


Figure 2.12: Design pattern created with the solid work with 1mm height of each layer.

Table 2.3: Power and Energy density of printed SCs.

Sample	Specific Current of GCD[A/g]	Power Density [W/kg]	Energy density [Wh/kg]
Commercial Ink	1	906	17.1
LASiS Synthesized Ink	1	1002	32.8

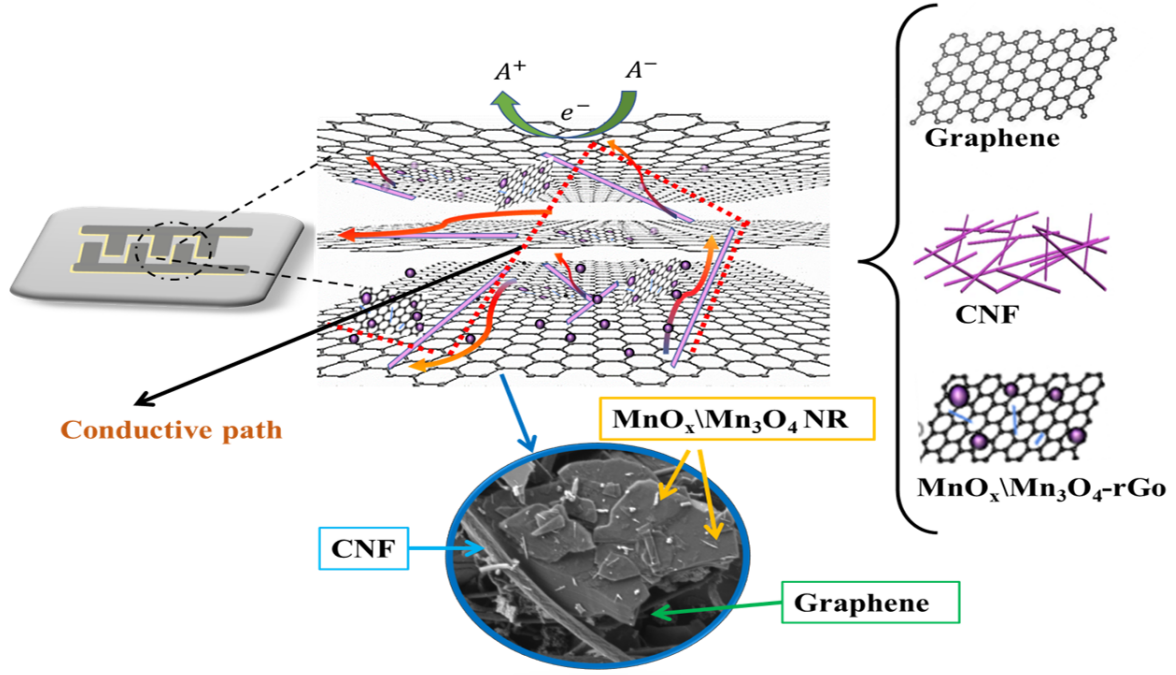


Figure 2.13: Schematic illustration of the percolated conductive network of CNFs, $\text{MnO}_x/\text{Mn}_3\text{O}_4\text{-rGo}$ and graphene nanosheets.

$$I = \frac{\Delta Q}{\Delta t}, \Delta Q = \frac{I}{\Delta t} \quad (2.5)$$

$$C_p(\text{specific capacitance}) = \frac{I \Delta t}{m \Delta V} = \frac{I_m \Delta t}{\Delta V} \quad (2.6)$$

m is active mass of sample(g), $I_m = I/m$ is current density (current per unit mass)

For 2-electrode system:

$$C_p(\text{specific capacitance}) = 2 \times \frac{I_m \Delta t}{\Delta V} \quad (2.7)$$

Δt is discharge time

ΔV is potential drop = $V_2(\text{peak}) - V_1(\text{lower})$

Energy density E_g :

$$E_g = \frac{\frac{1}{2} C_p \Delta V^2}{3.6} (\text{Wh kg}^{-1}) \quad (2.8)$$

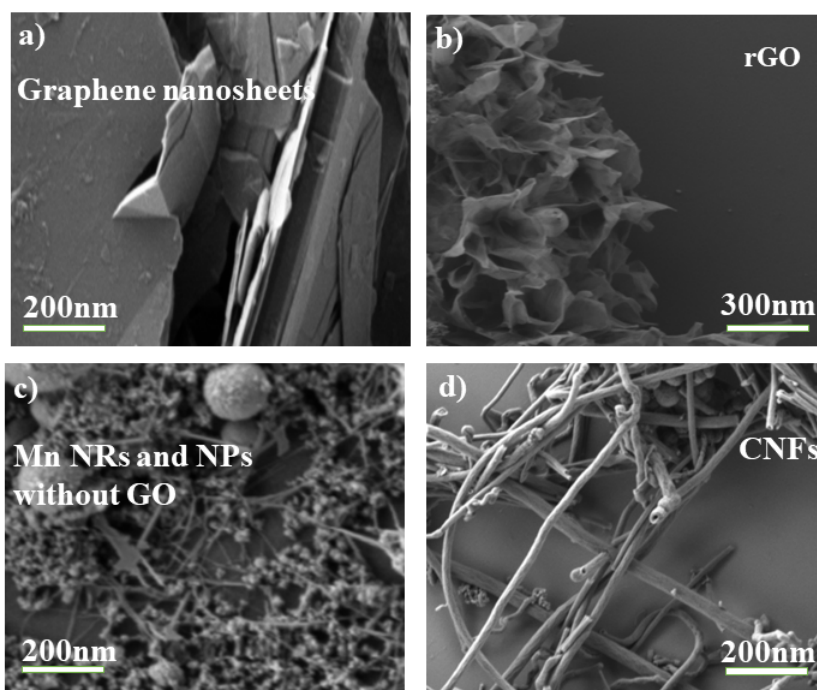


Figure 2.14: NRs and NPs synthesized after ablation in DI H₂O without GO solution.

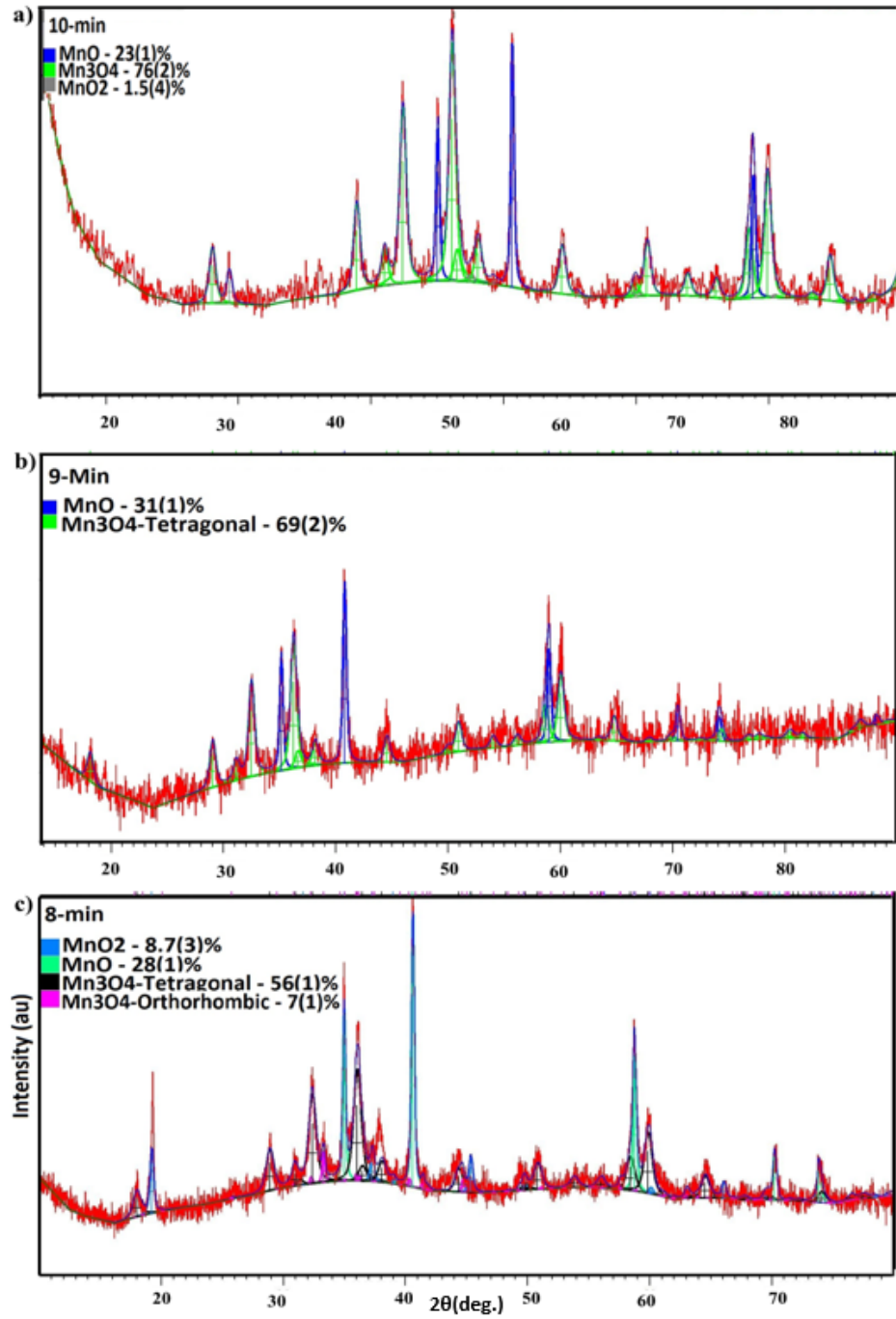


Figure 2.15: XRD peak patterns for samples prepared at (a) 10-, (b) 9- and (c) 8- mins ablation time.

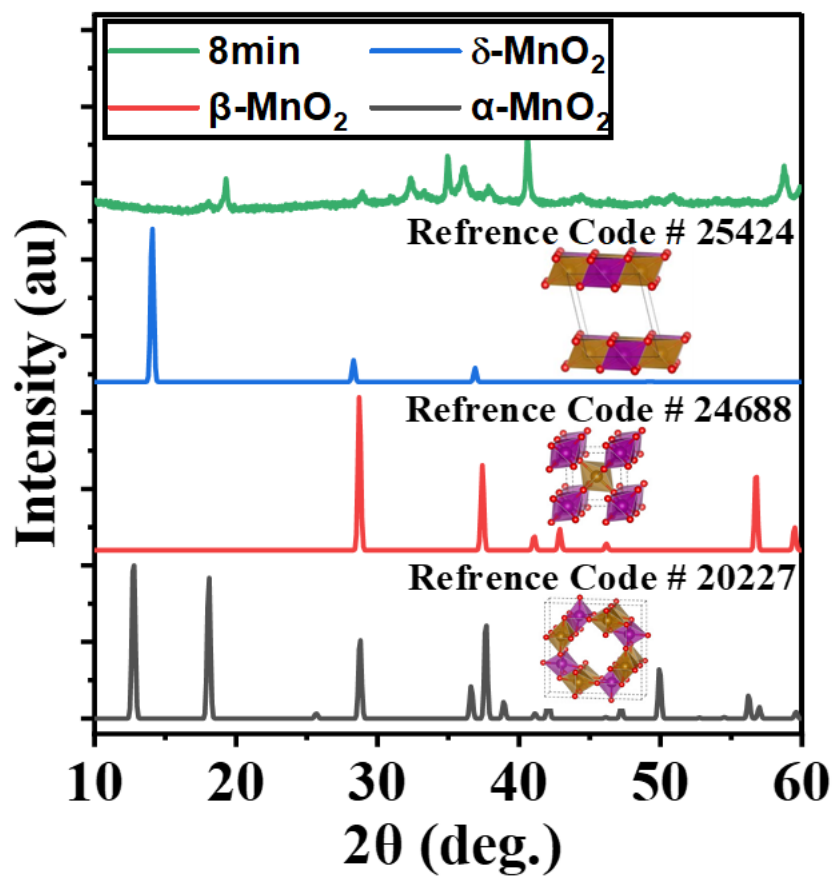


Figure 2.16: XRD pattern of the Laser derived MnO_x/Mn₃O₄-rGO HNCs prepared under 8 min ablation time and comparison with standard XRD pattern of α -, β - & δ -MnO₂.

Power density P_g :

$$P_g = \frac{E_g \times 3600}{\Delta t} (W kg^{-1}) \quad (2.9)$$

For synthesized Ink, printed SC

At $A=1A/g$

$\Delta t = 125$

$C_s = 2 \times 125 \times 1/1 = 250 \text{ F/g}$

$E_g = [1/2 \times 325 \times (0.8)^2] / 3.6 = 32.8 \text{ (Wh kg}^{-1}\text{)}$ Higher: greater the amount of energy it has stored)

$P_g = [32.8 \times 3600] / 125 = 1002.12 \text{ W kg}^{-1}$

For commercial Ink, printed SC.

At $A=1A/g$

$\Delta t = 80$

$C_s = 2 \times 80 \times 1/1 = 158 \text{ F/g}$

$E_g = [1/2 \times 158 \times (1)^2] / 3.6 = 17.1 \text{ (Wh kg}^{-1}\text{)}$

$P_g = [17.1 \times 3600] / 80 = 906 \text{ W kg}^{-1}$

XRD patterns of Figure 2.15 indicate that various manganese oxide structures could be detected in the nanocomposites structure formed during the LASiS-induced synthesis of the HNCs. XRD patterns of samples prepared under 9- and 10- mins of ablation times ((a)&(b)) indicate negligible presence of MnO_2 crystal structures in the HNCs structure while its mass ratio for the sample prepared under 8- mins ablation time is around 9%. Also, Figure 2.16 shows a distinct peak for α - MnO_2 around $2\theta=18$ and $2\theta=39$ (deg).

2.8 summary

In this study, the supercapacitive properties of HNCs comprised of rGO interfaced with nanostructured MnO_x/Mn_3O_4 synthesized *via* Laser Ablation Synthesis in Solution (LASiS) using various ablation times (6-10 minutes) in tandem with a post-processing thermal annealing process is investigated. Detailed structural characterizations revealed that the electroactive nonstructures embedded in the rGO 2D matrices are primarily composed of MnO_x/Mn_3O_4 species with varying mass concentrations (wt%) of MnO, MnO_2

and Mn_3O_4 oxide phases. Functional characterizations demonstrated the influence of varying ablation times during the LASiS process on the structure-composition properties of the ensuing HNCs— namely, in the form of the optimal concentration ratios for: 1) $\text{rGO:MnO}_x/\text{Mn}_3\text{O}_4$ NRs, and 2) $\text{MnO:MnO}_2:\text{Mn}_3\text{O}_4$ structures (wt%) which, in turn, govern the characteristic capacitive behaviors of the HNC-based electrode inks. Specifically, electrochemical characterizations indicated that HNCs samples carrying significantly higher MnO_2 contents (~ 9 wt%) in the $\text{MnO}_x/\text{Mn}_3\text{O}_4$ NRs, and prepared under 8-minute ablation time, exhibited the highest supercapacitive properties with capacitance of ~ 442 F/g. We also implemented direct inkjet printing techniques for the successful fabrication of advanced SC electrodes comprising the active layer ink composed of HNC-based electroactive materials interfaced with a percolated conductive network of electronic grade Graphene nanosheets and CNFs. In conclusion, the electrochemical characterization of the all-printed SC electrode material fabricated from LASiS-derived $\text{MnO}_x/\text{Mn}_3\text{O}_4\text{-rGO}$ HNCs showed a higher specific capacitance of $C_{sp} \sim 325$ F/g owing to higher surface area and redox reactions, as compared to standard commercially-made $\text{Mn}_3\text{O}_4\text{-Graphene}$ NCs ~ 189 F/g.

Chapter 3

Facile Synthesis of Non-Precious Bimetallic Zeolitic Imidazolate Framework-Based Hierarchical Nanocomposites as Efficient Electrocatalysts for Oxygen Reduction Reaction

This chapter is based on the submitted and published article: *"Facile Synthesis of Nonprecious Bimetallic Zeolitic Imidazolate Framework-Based Hierarchical Nanocomposites as Efficient Electrocatalysts for Oxygen Reduction Reaction"* by Mahshid Mokhtarnejad, Erick. L. Ribeiro, Dibyunde Mukherjee, and Bamin Khomami.....
DOI: 10.1021/acsanm.3c02703

Conversion of designer metal-organic frameworks (MOFs) into hybrid nanocomposites (HNCs) consisting of transition metal/metal oxides interfaced with carbon (C) matrices has

emerged as a promising and economical alternative for the synthesis of oxygen reduction reaction (ORR) electrocatalysts, owing to their superior conductivity and high porosity. To that end, optimizing the performance of this class of material by tailoring their composition, structure, size, and morphology through an efficient synthesis route has become an active area of research. Specifically, this study employs Laser Ablation Synthesis in Solution in tandem with Galvanic Replacement Reaction (LASiS-GRR) technique as an environmentally friendly, facile, and rapid route for the design and synthesis of core-shell bimetallic Zeolitic Imidazolate Framework (ZIF) heterostructures as bi-MOFs, and their pyrolytic post-processing to yield hierarchical metal oxide/MOF-based functional HNCs as highly active ORR electrocatalysts. The LASiS-GRR technique employs high-energy laser plasma reactions as the rate-controlling step for initiating solution-phase galvanic reactions. The one-pot, two-step process introduced in this study enables tailoring the composition, structure, size, and morphology of composite bi-MOFs comprising Co-based MOFs encapsulated in Zn-based porous crystals (Co/ZIF-67@Zn/ZIF-8). Pyrolytic post-processing of these core-shell bi-MOF crystals leads to the creation of hierarchical ZnO@ZIF/C HNCs with superior ORR electrocatalytic performances under alkaline conditions. Overall, these findings not only elucidate the process by which LASiS-GRR protocols are optimized to tailor the morphology, structure, and composition of complex MOF structures but also demonstrate the superior performance and stability of the ensuing post-pyrolyzed ZnO@ZIF/C HNCs as non-precious metal-based ORR electrocatalysts, when compared to commonly used Pt- and Pt-group metals (PGM)-based electrocatalysts.

3.1 Introduction

Rapid progress in the synthesis of functional nanomaterials (NMs) has paved the way for the development of novel nanostructured materials (NSMs) for a host of applications. Consequently, promising top-down and bottom-up synthesis techniques for the synthesis of functional metal nanoparticles (NPs) have been developed [118]. Top-down techniques, such as milling, sonication, lithography, and gas-phase quenching of heated bulk metal, lack

rational control over the size, morphology, and structure of NPs. On the contrary, bottom-up approaches, which involve the assembly of atoms, molecules, and clusters to engineer NPs, offer more control over structure and size [82, 1]. However, these techniques are often complex and time-consuming. Most common bottom-up methods for synthesizing colloidal NPs include electrochemical[47], sonochemical [91], microwave radiation[20], radiolytic[43], and photochemical [107] techniques that rely on chemical reduction of diverse precursor salts in aqueous and non-aqueous solvents.

Among these methods, Laser Ablation Synthesis in Solution in tandem with Galvanic Replacement Reaction (LASiS-GRR) [54, 88, 89] is a promising facile technique for the synthesis of NPs and hybrid nanocomposites HNCs. This technique is rapid, dependable, and continuous and does not require the use of harsh chemical reagents, surfactants, nor continuous monitoring of cumbersome steps, unlike most wet chemical reduction routes. To that end, in recent years functional nanomaterials with diverse structures, morphologies, and compositions have been synthesized via LASiS-GRR. This includes the synthesis of intermetallic nanoalloys [51], and nanocomposites as electrocatalysts [52], as well as graphitic C-coated shell-core Al NPs as energetic materials [25]. Moreover, LASiS-based techniques have proven successful in facile fabrication of Co-Oxide/Hydroxide nanostructures[53], Metal-Organic Frameworks (MOFs) [103] and MOF-derived HNCs [104, 86]. An inherent advantage of LASiS-GRR is that the high-temperature/pressure laser-induced plasma under liquid confinements can promote non-equilibrium reaction pathways with fast kinetics and quenching by the liquid environments that are otherwise not possible via traditional wet chemistry routes. To that end, LASiS-GRR has increasingly gained prominence as an attractive and expeditious method for reproducible and cost-effective synthesis of multi-elemental composite nanomaterials with complex structures.

In particular, MOFs form a unique class of high-porosity hybrid nanomaterials (HNMs) with 3D frameworks that have increasingly found broad applicability for gas and energy storage, sensing, and drug delivery [85, 28, 67, 135]. In particular, zeolitic imidazolate frameworks (ZIFs) belong to a class of MOFs that - due to their large surface area, porosity, and high density of transition metals - show great promises for the engineering of Oxygen Reduction Reaction (ORR) electrocatalysts for fuel cells including Alkaline

Anion Exchange Membrane Fuel Cell (AEMFCs) [74]. Additionally, MOF encapsulations in protective matrices or coatings have been extensively employed in recent years to mitigate the degradation of catalysts over time and improve their long-term performance in an effort to enhance the stability and durability of MOF-based ORR catalysts. [131]. Until now, the commonly known ORR electrocatalysts of choice have been platinum (Pt)- and platinum group metals (PGM)-based NPs. These high-performance electrocatalysts can facilitate a four-electron transport pathway with reduced overpotentials during ORR in AEMFCs [120]. Despite these benefits, the price of Pt and its poor stability under harsh alkaline conditions have motivated research on the development of low-cost, high-performance ORR electrocatalysts that can replace Pt in a host of energy storage and conversion devices [62]. To that end, a host of recent studies have focused on the synthesis of various functional HNCs as ORR electrocatalysts. The fabrication of MOF-derived HNCs as catalysts to replace expensive Pt-based NPs often involves complex chemical synthetic routes with precise control of the synthesis parameters. Traditional chemical methods require highly involved experimental setups and the use of harsh reagents and surfactants/capping agents to prevent aggregation/coalescence while allowing surface functionalization. But, in turn, these surfactants can pose significant challenges for the desired interfacial activities on catalytic surfaces. Furthermore, time-consuming, and cumbersome processes involving multiple preparation and purification steps in wet chemistry routes and the generation of significant waste pose challenges for rapid, sustainable, and large-scale synthesis. Therefore, the development of a facile, rapid, and direct method for the reliable and efficient synthesis of stable and durable MOF-based ORR electrocatalysts remains an area of great interest [119].

This study presents an efficient and rapid synthesis route for Co-based MOFs encapsulated in Zn-based porous MOFs (Co/ZIF-67@Zn/ZIF-8) *via* LASIS-GRR, followed by post-pyrolytic treatment to form HNCs of ZnO nanorods (NRs)-interfaced ZIF-67 in carbonaceous matrices that exhibit superior ORR electrocatalytic activity in alkaline media. LASIS-GRR is a low-cost, simple, and environmentally friendly alternative for synthesis of MOF-based HNCs. Specifically, we elucidate the influence of different precursor salts in a tandem galvanic reaction on the size and morphology of these HNCs and their electrocatalytic activity.

Notably, we demonstrate the potential of these MOF-based electrocatalysts consisting of earth-abundant metals such as Zn and Co to surpass the performance of conventional Pt- and PGM-based ORR catalysts.

3.2 Experiment and Methodology

3.2.1 LASiS-GRR synthesis of MOF and bi-MOFs

The process involves laser ablation of a metal target in a liquid during LASiS, resulting in the formation of a laser-induced plasma plume at the solid-liquid interface. The elevated temperature and pressure of the plasma create a unique medium for chemical reactions, enabling the synthesis of unique material phases by combining the liquid phase and target elements. Post ablation, the plasma cools down and depressurizes, leading to cluster growth and the fabrication of desired NPs and nanocrystals [115]. Unlike conventional nanofabrication techniques that require specific control of synthesis parameters such as pressure and temperature [112], LASiS [104, 55] is a simple, non-toxic, environmentally friendly and cost-effective technique for nanomaterial production. The underlying physico-chemical processes that lead to rational synthesis of a broad range of NMs *via* the LASiS-GRR are presented in our previous publications [88, 89, 52, 55, 51, 54, 103, 104, 86].

In this study, we have adopted the LASiS-GRR technique (schematically illustrated in Figure 3.1) to rapidly fabricate MOF-based functional bimetallic HNCs as Pt-free ORR electrocatalysts in an alkaline medium. We obtained the requisite starting material from Sigma-Aldrich and Kurt J. Lesker (1/4" diameter with 1/4" height Zinc (Zn) pellets with 99.5 percent purity). We used an unfocused high-energy pulsed Nd-YAG laser to ablate the Zn target for ten minutes. To adjust the solution pH to the desired value, namely pH=13, we added Potassium Hydroxide (KOH, > 99%) to the solution. Two concentrations of Cobalt(II) (*i.e.*, Cobalt(II) nitrite, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Cobalt(II) chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (>99.9%)) solutions (11 mg/L) were prepared by dissolution of a specific amount of salt in 35 mL of potassium hydroxide solution (3 M potassium hydroxide in deionized (DI) water). To examine the role of precursor salts in tailoring the size and morphology of NPs and the

final product, we used the previously mentioned precursor salts. Finally, we added 1.7 g of 2-methylimidazole (Hmim) to each solution.

The LASiS procedure begins by transferring the solution to the reactor cell through the injection unit, followed by ablation of the Zn metal target using a 1064 nm pulsed Nd-YAG laser (310 mJ/pulse, 10 Hz duration) for ten minutes. To ensure complete crystallization of MOFs with their inherent low kinetic rate of nucleation and crystallization, we kept the suspension at room temperature for 24 hours. The laser-synthesized products were subsequently centrifuged at 4700 rpm for 20 minutes and decanted by washing them with deionized water followed by a methanol washes (three times) to remove any unreacted chemical precursors. Eventually, Co/ZIF-67@Zn/ZIF-8 samples with different morphologies form from the initial 11 mg/L concentrations of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solutions. For comparison purposes, a Co-free MOF (Zn/ZIF-8) was prepared using the same procedure but without the addition of the cobalt precursor. Finally, we synthesized a Zn-free MOF (Co/ZIF-67) using a solution with cobalt precursor salt, without employing a Zn metal target during LASiS. This allowed us to evaluate the impact of the precursor salt during laser ablation and the successful synthesis of the Zn-free MOF (Co/ZIF-67).

Pyrolytic post-treatments: To synthesize bimetallic ZnO@ZIF/C and ZnO/C HNCs, the products obtained after centrifugation and methanol washes were pyrolyzed under N_2 atmosphere at different temperatures, guided by TGA data, for a duration of 2 hours (details provided in Figure 3.9). After the pyrolysis process, we cooled samples to room temperature by leaving them in ambient air for 12 hours. In turn, we performed extensive characterization of the resulting ZnO@ZIF/C and ZnO/C nanocomposites, obtained respectively from the pyrolysis of Co/ZIF-67@Zn/ZIF-8 and Zn/ZIF-8.

3.2.2 Structural, compositional, and morphological characterization of MOFs and HNCs

Initially, we employed two techniques to characterize the structure and composition of the synthesized samples: 1) X-ray diffraction (XRD) with a Phillips X’Pert-Pro diffractometer with a Cu $\text{K}\alpha$ monochromatized radiation source ($\lambda = 0.1541 \text{ nm}$) functioning at 45 kV, and

40 mA, and 2) A Nicolet iS50 FTIR spectrometer device with an absorption spectra range of 5000-400 cm^{-1} . In turn, microscopy and elemental mapping were carried out using: (1) a Philips XL-30ESEM scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX) spectroscopy and Helios 5UX dual beam FIB/SEM to acquire SEM-EDS micrographs, and (2) transmission Electron Microscope (TEM) using a JEOL JEM 1400-Flash and Thermofisher Tecnai Osiris scanning/transmission electron microscope (S/TEM) operated at an accelerating voltage of 120 kV. We also obtained Raman spectra using an NT-MDT NTEGRA spectra instrument with a 532 nm green laser beam. Finally, we performed thermogravimetric analysis (TGA) on a standard TA instrument (Q50 15GA) in an inert N_2 environment, by heating the samples from ambient temperature to 900 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$. This information was in turn utilized to determine the optimal pyrolysis temperature and thermal properties of the Laser-derived Co/ZIF-67@Zn/ZIF-8 and Zn/ZIF-8. Collectively, these characterization techniques confirm the successful preparation of novel laser-derived core-shell MOFs, bi-MOFs, and HNCs as electrocatalysts.

3.2.3 Electrochemical characterization

We performed electrochemical characterization with a cell consisting of a rotating disk electrode (RDE) from Pine Instruments LLC. The electrochemical cell has a three-compartment configuration, with a saturated double-junction Ag/AgCl electrode serving as the reference electrode and a platinum (Pt) coil serving as the counter electrode. The hydrogen electrode (RHE), serves as the standard reference for all electrochemical measurements.

Oxygen reduction reaction (ORR) tests

To measure the ORR activity, we used a glassy carbon rotating disk electrode (RDE) with a diameter of 5 mm and a 1 M KOH solution as the working electrode and electrolyte, respectively. As a benchmark for the performance and stability comparison, we employed a commercially available state-of-the-art electrocatalyst consisting of 20 wt.% platinum on Carbon (BASF SE). Electrocatalyst inks were prepared by dispensing 2 mg of the chosen synthesized HNCs in a mixture of 25 μL of 5 wt.% Nafion and 1 mL ethanol solution.

Subsequently, we deposited 6 μL of the ink on the RDE to create an electrocatalyst layer with a density of approximately 30 $\mu\text{g}\cdot\text{cm}^{-2}$. To assess the electrocatalytic performance, we analyzed the rotating disk voltammetry (RDV) at various rotation speeds using the Koutecky-Levich (KL) equation (Equation 1).

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_k} + \frac{1}{B\omega^{\frac{1}{2}}} \quad (3.1)$$

$J_K = nFkC_0$; $B = 0.62nFC_0D_0^{2/3}\nu^{-1/6}$, where J is the total current density, J_K is the kinetic limiting current density, and J_L is the diffusion limiting current density; n depicts the number of transferred electrons, F denotes the Faraday constant, C_0 is dissolved O_2 concentration, and D_0 is the O_2 diffusion coefficient in the electrolyte; ν represents the rotational rate of the electrode in revolution per minute (rpm). Kinetic currents J_K for all Tafel plots were derived from equation (2):

$$J_K = \frac{J \times J_L}{J_L - J} \quad (3.2)$$

3.3 Results and discussion

In what follows, we present a comprehensive characterization of LASiS-driven synthesis of nano-porous Zn/ZIF-8 MOF, core-shell Co/ZIF-67@Zn/ZIF-8 bi-MOF structures, and ZnO/C and ZnO@ZIF/C HNCs. In turn, we utilize our experimental results to establish the relationship between the synthesis, structure, and properties of the synthesized MOFs and HNCs. In the following sections, we provide a summary of the materials and their electrochemical properties, highlighting their unique features and performance. Notably, this study documents the first-ever one-pot LASiS-driven synthesis of two distinct ZIF structures, namely Co/ZIF-67@Zn/ZIF-8 by simply adjusting the precursor concentration of the Co salt in the solvent with the same laser-driven synthesis protocol. This breakthrough demonstrates the versatility of the LASiS technique in tailoring the morphology, composition, and structure of MOFs, opening up new possibilities for advanced material synthesis.

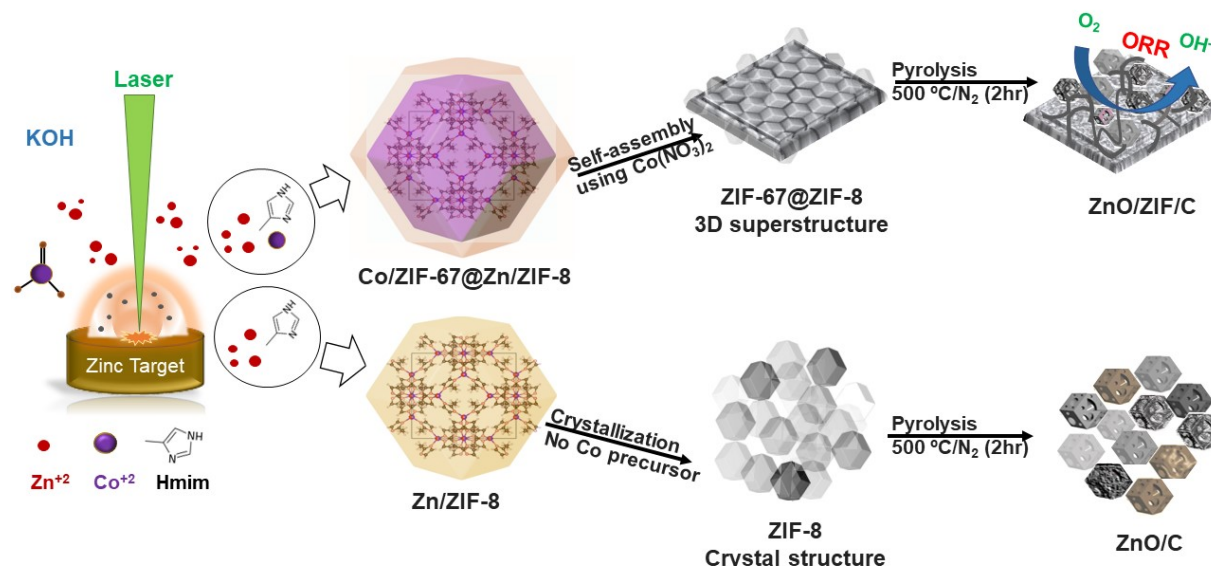


Figure 3.1: Schematic illustration of LASiS methodology used to synthesize bimetallic MOF-derived electrocatalysts.

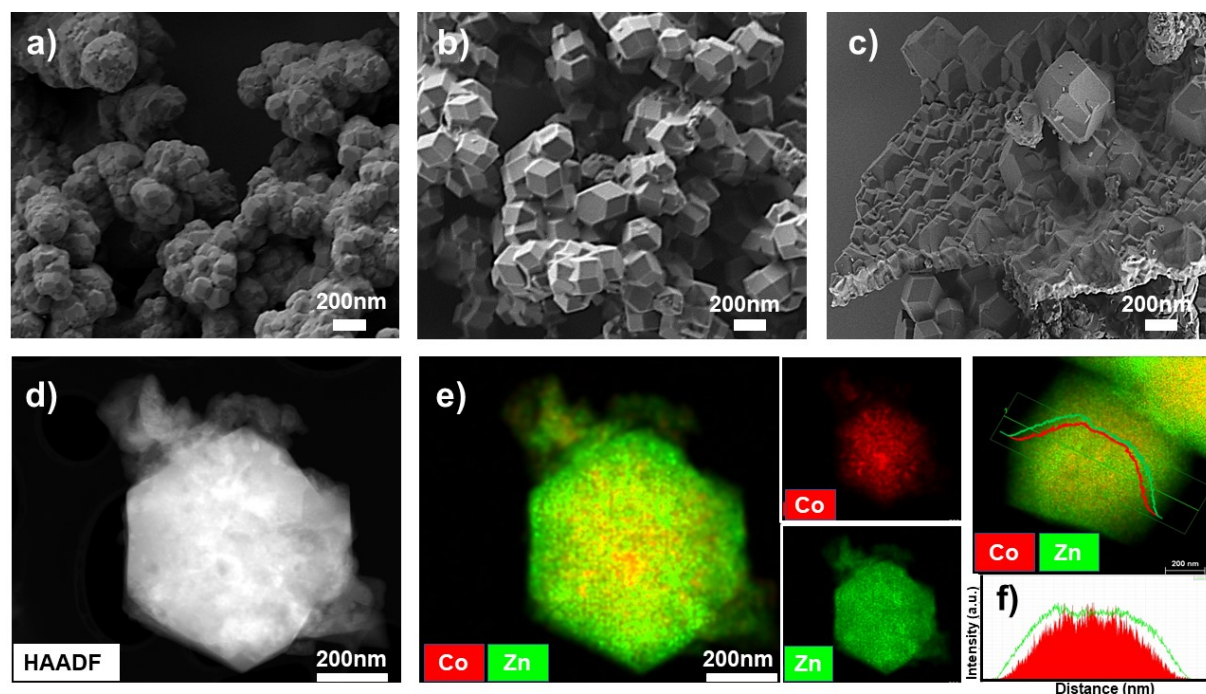


Figure 3.2: SEM micrographs of (a) Zn/ZIF-8, (b) Co/ZIF-67@Zn/ZIF-8 using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ precursor salt, (c) Co/ZIF-67@Zn/ZIF-8 using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor salt, synthesized at pH13; STEM and elemental mapping micrographs of (d-f) Co/ZIF-67@Zn/ZIF-8 using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor salt.

3.4 Structural and morphological characterizations of LASiS-derived MOFs

In this section, we explore the intricacies of LASiS-GRR synthesis protocol to tailor the shape, size, and morphology of the as-synthesized MOFs, as well as the formation of HNCs post pyrolysis. Specifically, we demonstrate that by tuning solution-laser-phase parameters, such as reagent concentration, and laser properties, namely, ablation time and pulse energy, one can control the assembly of the final polyhedral MOFs. Specifically, we present the parameter space for synthesizing MOF nanostructures with long-range, three-dimensional, semi-ordered, membrane-shaped superstructures. To that end, the obtained results encompass the morphology, composition, size, and structure of the as-synthesized porous MOFs and HNCs, characterized using diverse complementary techniques. Figure 3.2 depicts SEM images of Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 samples prepared using different precursor salts at pH 13 before pyrolysis. SEM images (Figures 2(a and d)) illustrate the formation of interconnected rhombohedral ZIF-8 crystal structures with dimensions in the range of few hundred nanometers. To that end, synthesis in an alkaline solution of pH 13, without use of any precursor salt (see Figure 3.2(a)) leads to agglomeration and a commensurate increase in the size of the rhombohedral structures. On the contrary, 10-minute ablation with 11 mg/mL of different Co precursor salts $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Figure 3.2(b)) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Figure 3.2(c)), results in a morphology transition. Specifically, the regular polyhedral structures for the Co/ZIF-67@Zn/ZIF-8 crystals (Figure 3.2(b)) transform into a semi-ordered rhombohedral structure assembled onto membrane-shaped superstructures composed of the MOF NPs. These long-range structures appear as a result of synthesis under alkaline conditions (pH 13) using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the precursor salt (Figure 3.2(c)). The differences in reaction rates resulting from the decomposition of different precursors leads to formation of different morphologies in the final MOF structures [45, 39]. The elemental mapping images and line scanning spectra from EDS measurements depicted in Figures 2(d-f), provide clear visual evidence of core-shell heterostructures in the as-synthesized bi-MOFs. The EDS elemental mapping scan in Figure 3.2(e) confirms the high concentration of Co at the core, and uniformly distributed Zn throughout the

sample. These observations verify the successful formation of core-shell structures in the Co/ZIF-67@Zn/ZIF-8 bi-MOFs. Moreover, the EM-EDS cross-sectional line-scan analysis in Figure 3.2(f) obtained along a linear path traversing the peripheral and central regions of a representative bi-MOF as shown in the figure. The spectrum indicates higher Co-contents toward the center, with an increase in Zn-contents toward the periphery of the bi-MOF structures. This further corroborates the hypothesized core-shell structures of the bi-MOFs. (See Figure 3.10 for more detailed micrographs). The morphologies of LASiS-GRR-prepared ZIFs are more diverse than ZIF-67 and ZIF-8 synthesized via conventional hydrothermal route. To that end, LASiS-GRR offers advantages in terms of rapid synthesis and control over the composition of the resulting materials. In fact, the ability to create these unique morphologies such as MOF-based 3D superstructures play a pivotal role in optimizing their functionalities such as their electrocatalytic performance.

SEM and XRD analysis (see Figures 2 and 3) confirm that the choice of Co(II) salt precursors affect the size and shape of bimetallic Co/ZIF-67@Zn/ZIF-8 MOFs synthesized at pH 13. We rationalize the observed variations in different crystal sizes based on the nucleophilic reactivity of the counter anions to the metal cations. Specifically, the higher electronegativity of chloride (Cl^-) compared to nitrate ($(\text{NO}_3)^-$) results in nitrate exhibiting higher nucleophilic reactivity. We postulate that this difference in reactivity leads to lower solvation of nitride, which in turn leads to the formation of membrane-shaped crystals with a smaller crystallite size. Specifically, the decreased solvation of nitrate leaves fewer metal cations in the solution for oligomerization, which occurs through the bridging of metal centers and *via* deprotonated imidazole. Similar morphological in wet chemistry hydrothermal synthesis of MOFs have been documented[5, 69]; however, this is the first study to document these morphological transitions in LASiS-GRR synthesized MOFs.

In what follows, we discuss the results of our detailed structural characterizations of the previously mentioned MOF samples, focusing on XRD analyses (see Figure 3.3(a)) for Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 samples. To this end, the presence of sharp and distinctive peaks in the LASiS-made Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 MOF samples which closely match the simulated diffraction patterns of ZIF-8 and ZIF-67 [73], confirms the existence of highly crystalline ZIF-67@ZIF-8 phases. Since the simulated diffraction

patterns of ZIF-8 and ZIF-67 are identical, decoupling ZIF-8 peaks from the Zn/ZIF-8 structures in the presence of both ZIF-8 and ZIF-67 in the Co/ZIF-67@Zn/ZIF-8 structures are challenging. However, a slight shift to lower 2θ values in XRD peaks indicates smaller pore sizes of Co/ZIF-67@Zn/ZIF-8 bi-MOF as compared to the Zn/ZIF-8 MOF sample (Figure 3.3(a) and 3.8). Also, FTIR measurements identify the effective surface-specific functional groups present in these as-synthesized MOFs. Figure 3.3(b) depicts the spectral features of the Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 MOFs. The spectral bands found at 756 cm^{-1} are due to the 2-Methylimidazole (Hmim) out-of-plane bending ring, whereas the peaks at 1424 cm^{-1} are due to the in-plane bending [2]. Strong C-N vibrations at 1310 cm^{-1} , and the C=N vibration at 1594 cm^{-1} [122, 57]. The strong C-N vibrations at 1310 cm^{-1} , and the C=N vibration at 1594 cm^{-1} is indicative of Hmim presence as a linker in the ZIF-8 structure [122, 57]. In general, the peak at $1250\text{-}1020\text{ cm}^{-1}$ is indicative of C-N stretching, and at $1650\text{-}1580\text{ cm}^{-1}$ is a signature of NH vibrations in the same structure or due to NH bending in the Hmim molecule. Furthermore, the stretching of the Hmim aromatic ring is responsible for the weak peak at 1630 cm^{-1} . The strong metal-linker bond such as Co-N or Zn-N at 434 cm^{-1} confirms the presence of metal centers in Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 MOF structures [105]. Moreover, localized SEM coupled with EDX spectroscopy (SEM-EDX) measurements (see Figure 3.3(c)) unequivocally demonstrate the presence of the respective Zn and Co metal nodes in Co/ZIF-67@Zn/ZIF-8 and Zn/ZIF-8 MOF samples. These analyses clearly show that the Co/ZIF-67@Zn/ZIF-8 structures exhibit both characteristic Co peaks for the $K\alpha = 6.9\text{ keV}$ and $L\alpha = 0.78\text{ keV}$ transitions and Zn peaks for the $K\alpha = 8.63\text{ keV}$ and $L\alpha = 1.01\text{ keV}$ transitions. These SEM-EDX images provide direct evidence of the presence of Zn and Co in the bi-MOF structures along with Carbon (C) and Nitrogen (N) arising from the Hmim linkers in the ZIF structures. Also, the peak from the $K\alpha = 1.74\text{ keV}$ transition arises from the silicon (Si) holder substrate used to immobilize MOFs during SEM-EDX analysis. Finally, Figure 3.7 depicts the formation of Co/ZIF-67 immediately after the laser heats a solution that only contains the Co precursor salt and Hmim, *i.e.*, without a metal target. Specifically, the polyhedral Co/ZIF-67 crystals start to grow when the laser ablates the solution with a precursor salt and linker (Figure

3.7(b)), which in turn verifies the formation of Co/ZIF-67 encapsulated in Zn/ZIF-8 to form Co/ZIF-67@Zn/ZIF-8 bi-MOFs.

Figure 3.4(a) depicts various stages of MOF formation resulting from the solution-phase reactions for Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8. Upon exposure to a high-energy laser pulse, the metal pellet vaporizes and, in turn, forms a plasma plume with extreme temperatures and pressures. This leads to the oxidation of Zn ions in the solution according to their respective redox potentials: ($\text{O}_2 / \text{OH}^{-1} \sim 0.40 \text{ V vs. SHE}$) / ($\text{Zn} / \text{Zn}^{+2} \sim -0.7618 \text{ V vs. SHE}$). Likewise, immediately after the high-energy laser pulse heats up the solution, the formation of Co/ZIF-67 MOFs ensues (see Figures S1 and 5(b)). Zn^{+2} ions resulting from laser ablation serve as the ionic precursors for the reaction pathway that leads to the emergence of Zn/ZIF-8 crystals which in turn encapsulates the synthesized Co/ZIF-67 MOFs (Figure 3.7) to create Co/ZIF-67@Zn/ZIF-8 structures. Therefore, as shown in Figure 3.4(a), 4 hours post-ablation, ionic Zn metals start to form the ZIF-8 structure, which yields a dense white solution in the Zn/ZIF-8 case and the dense purple solution in the case of the Co/ZIF-67@Zn/ZIF-8 samples. After a 24-hour period at room temperature, the undisturbed solution contains a precipitated solid phase. Figure 3.4(b) shows the Transmission Electron Microscopy (TEM) micrographs of highly porous Zn/ZIF-8 scaffolds and dense Co/ZIF-67@Zn/ZIF-8 MOFs. Specifically, Figure 3.4(b) depicts the regions with different contrast indicating the high porosity of Zn/ZIF-8 compared to Co/ZIF-67@Zn/ZIF-8 sample. The encapsulation of Co/ZIF-67 MOFs in Zn/ZIF-8 structures create a porosity difference between Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 structures (Figure 3.1 and Table 3.1).

Therefore, the Co/ZIF-67@Zn/ZIF-8 formation using a cobalt precursor salt and a Zn metal target consists of four primary stages:

1. Coordination of cobalt (Co^{2+}) metal centers by the imidazole molecules immediately after the laser heats the solution to create ZIF-67 MOFs.
2. Coordination of Zn^{2+} centers (derived from ablation of Zn metal target) by the remaining Hmim molecules to facilitate the growth of ZIF-8 molecules that encapsulate ZIF-67 NPs.

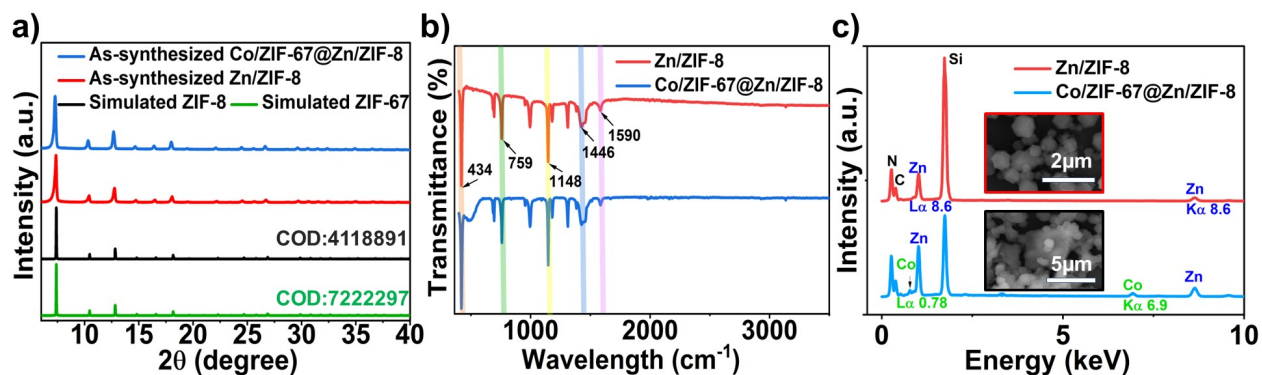


Figure 3.3: (a) XRD peaks $2\theta = 5-65$ (degree) highlighting various crystal planes, (b) FTIR spectrum within $400-4000 \text{ cm}^{-1}$ depicting various functional groups in Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 structures, (c) EDX spectra of Zn/ZIF-8 (black) and Co/ZIF-67@Zn/ZIF-8 (red) HNCs on a Si wafer.

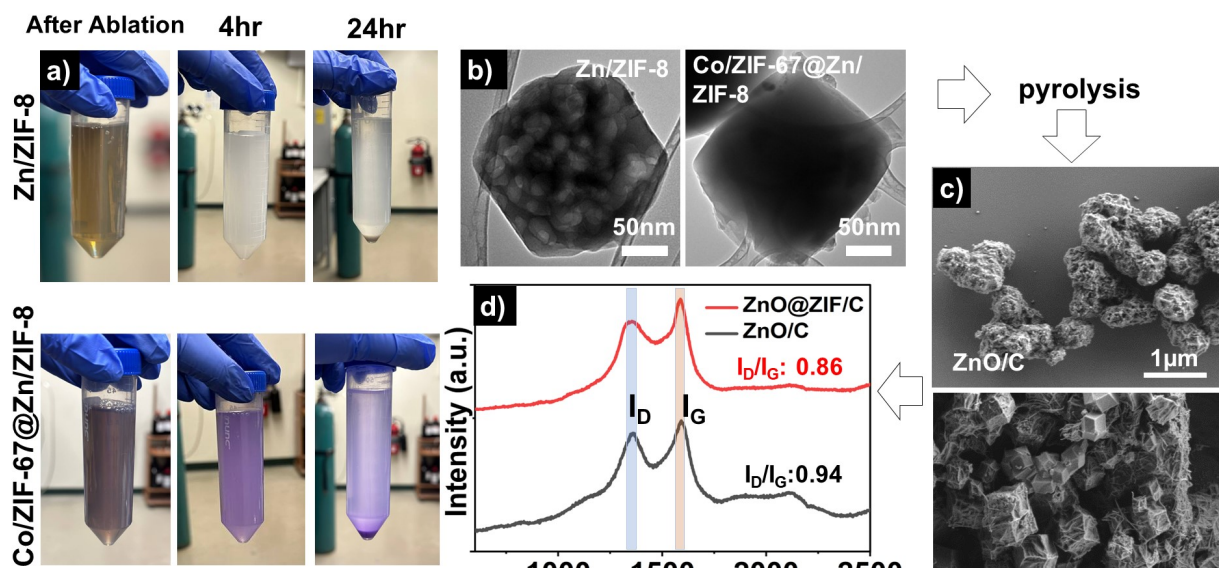


Figure 3.4: a) Co/ZIF-67@Zn/ZIF-8 and Zn/ZIF-8 MOFs formation before and after laser ablation, (b) TEM images of Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 HNCs, (c) SEM micrographs of ZnO/C and ZnO@ZIF/CHNC after pyrolysis, (d) Raman spectra of the ZnO@ZIF/C and ZnO/C HNCs from Co/ZIF-67@Zn/ZIF-8 and Zn/ZIF-8 HNCs, respectively.

3. Deprotonation of Imidazole; and ultimately,
4. Oligomerization by bridging separated Co^{2+} and/or Zn^{2+} centers *via* the deprotonated Imidazole.

To reproducibly engineer these MOFs and bi-MOFs, the ablation time is set to 10 minutes, and we fixed the concentration of cobalt nitrite at 11mg/mL. This leads to desired and reproducible concentrations of Co^{2+} and Zn^{2+} . This strict protocol allows for control of Co^{2+} and Zn^{2+} coordination and oligomerization rates that directly affect the final morphology and electrocatalytic performance of the as-synthesized HNCs.

3.5 Structural and morphological characterizations of post-pyrolytic HNCs

To identify the optimum temperature range for the pyrolysis of the Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 MOFs, TGA is employed. TGA results indicate an operating window from ambient temperature to 900 °C (see Figure 3.9). To that end, prior to the formulation of the ORR electrode inks, samples are pyrolyzed at 500 °C for 2 hours. Post-pyrolysis, the single-metal component Zn/ZIF-8 MOF samples create HNCs of ZnO nanostructures comprised of both nanoparticles (NPs) and nanorods (NRs) dispersed in a porous carbonaceous matrix (*i.e.*, ZnO@C), as seen from Figure 3.5(a). The SAED inset in the zoomed-out Figure 3.5(a) indicates the diffraction rings for the (100) plane of pure ZnO with a lattice spacing of $d = 2.8$ nm. Moreover, the XRD data for ZnO/C HNC samples, shown in Figure 3.5 (d), also indicate pure ZnO crystal peaks with a negligible amount of pure Zn. In contrast, the high-resolution TEM and STEM images in Figure 3.5(b) indicate that pyrolysis of Co/ZIF-67@Zn/ZIF-8 bi-metallic MOFs generates hierarchical structures comprising ZnO NPs/NRs coating the surfaces of a partially carbonized ZIF-67 polyhedron that are all embedded in a nano porous carbon matrix (*i.e.*, ZnO@ZIF/C). Also, the XRD data depicted in Figure 3.5(d) for the post-pyrolyzed ZnO@ZIF/C HNCs indicate the presence of both ZnO and standard ZIF-67 crystal peaks. We substantiate our claims for the formation of the previously mentioned ZnO nanostructures by high-resolution elemental mappings (see Figure 3.5(c)). These images

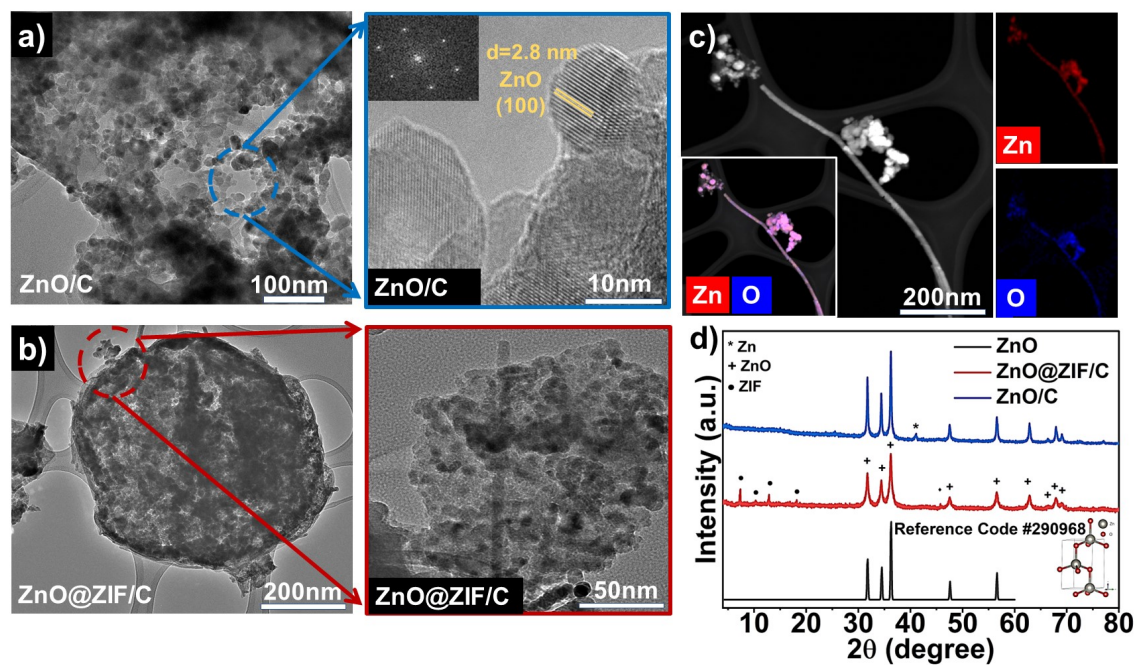


Figure 3.5: (a-b) TEM micrographs of ZnO/C and ZnO@ZIF/C HNCs, (c) STEM and elemental mapping micrographs of post-pyrolytic ZnO NRs and NPs, (d) XRD peaks $2\theta = 5-80$ (degree) highlighting the various phases in post-pyrolyzed ZIF and bi-ZIF.

clearly show the presence of a dense and uniform distribution of Zn and O elements in the NPs as well as NR-like structures in the post-pyrolytic samples.

In Figure 3.5(d), the high-intensity peaks in the spectrum of ZnO@ZIF/C HNC at $2\theta \approx 31.8, 34.5, 36.3, 47.6, 56.7, 63,$ and 68 correspond to ZnO phases in the structures formed post-heat treatment of Co/ZIF-67@Zn/ZIF-8 MOF. On the other hand, $2\theta \approx 7.3, 10.1, 12.8,$ and 18.1 are due to the existence of ZIF phases in the structure of ZnO@ZIF/C HNC. In summary, XRD data from ZnO@ZIF/C HNCs shown in Figure 3.5(d) shows distinctive ZIF-8 patterns, as well as crystalline zinc oxide (ZnO) phases. Hence, pyrolysis leads to the formation of a metal oxide@MOF-derived nano porous carbonaceous HNC. In contrast, in the case of ZnO@C, ZnO and a small trace of Zn phases are present, either due to the contamination in the system or a bulk metal left over from the laser ablation. Finally, Raman spectra of the ZnO@ZIF/C HNCs (see Figure. 4(d)) clearly illustrate the broad distinctive peaks at 1360 and 1582 cm^{-1} , corresponding to the D and G carbon peaks, respectively [106]. Specifically, A_{1g} vibration mode from phonon symmetry gives rise to the D peak, and the C_{sp^2} , in-plane vibration of sp^2 carbon atoms from E_{2g} phonon mode vibrations gives rise to the G peak. These findings indicate that carbon exists in both graphitic and amorphous phases. The D/G peak intensity ratios (I_D/I_G) shown in Figure 3.4(d) provide a good estimate of the amount of each phase in these materials [108]. A higher ratio (I_D/I_G) in ZnO/C HNCs ($I_D/I_G=0.94$) compared to ZnO@ZIF/C HNCs ($I_D/I_G=0.86$) signifies the presence of more disorder or defects resulting from the existence of amorphous.

3.6 Electrochemical and functional characterization of HNCs

For the cathodic and ORR electrocatalytic test, we used a 5 mm diameter polished carbon RDE with a 1 M KOH solution as the working electrode and electrolyte, respectively. Commercial platinum (Pt/C) (20%) from BASF Chemicals served as the standard catalyst for comparisons. To ascertain the ORR efficacy, we used standard linear sweep voltammetry (LSV) experiments. Although it is common to use 0.1 M KOH solution as the electrolyte for

ORR electrocatalyst experiments in alkaline environments, 1 M KOH electrolyte provides a more rigorous test of the performance and stability of the LASiS-based HNCs in extreme alkaline media. In addition to the challenges of establishing the robustness of the electrocatalysts in extremely corrosive electrolyte media, ORR operation in higher KOH concentrations is difficult because of the limited oxygen solubility and diffusivity of the alkaline electrolyte and the broader coverage of the electrocatalytic surfaces with alkaline species[62, 41]. Figure 3.6(a) shows the electrochemical data for the ORR electrocatalytic performances of the LASiS-derived HNCs plotted for the ZnO@ZIF/C, ZnO@C, and commercial Pt/C samples for comparison. Specifically, the plots include the test results for the hierarchical ZnO@ZIF/C and ZnO/C HNCs made from the respective pyrolysis of Co/ZIF-67@Zn/ZIF-67 bi-MOFs synthesized by using $\text{CoCl}_2/\text{Co}(\text{NO}_3)_2$ precursor salts, and Zn/ZIF-8 MOF synthesized without any precursor salts via LASiS. Commonly, the sample with the lowest overpotential has the best ORR electrocatalyst. Our results indicate that the hierarchical ZnO@ZIF/C HNC structures, when compared to standard Pt/C catalytic systems, exhibit the lowest overpotential of ~ 0.35 V vs. SHE relative to the standard reduction potential for $\text{O}_2/\text{H}_2\text{O} \sim 1.23$ V (corresponding to the half-wave potential of $E_{1/2} \sim 0.88$ V vs. SHE). Interestingly, we obtained these HNC samples through pyrolysis of Co/ZIF-67@Zn/ZIF-8 bi-MOFs synthesized via LASiS using $\text{Co}(\text{NO}_3)_2$ as the salt precursor under high-energy laser pulse (low Q-factor) with 10 minutes of ablation time and at pH 13 environment. Based on these observations, we can deduce that the oxygen reduction reaction (ORR) performance of the LASiS-derived hybrid nanocomposites (HNCs) is not solely determined by the hierarchical ZnO@ZIF/C structures. Rather, the significant interactions between the transition metal oxide nanostructures and the carbon (C) phases could potentially harness synergistic effects resulting from the metal nodes supported by ligands within the underlying ZIF scaffolds.

It is well known that O_2 activated on the C surface can provide radical oxygen intermediates, which can migrate into the metal oxide (MO_x)@MOF in the ZnO@ZIF/C matrix and in turn be reduced, to fulfill the standard 4-electron ($4e^-$) ORR path. For this reason, MO_x @MOF NMs are able to significantly enhance the ORR performance of the HNCs even at low concentrations. Therefore, the polarization curves show (Figure 3.6(a))

that ZnO@ZIF/C HNCs have the potential to outperform the Pt/C. In addition, one can tune the performance of this class of material by changing the sample morphology and size, as shown in Figure 3.2, as well as the precursor salt and pH of the solution. Figure 3.6(a) clearly demonstrates that among all prepared samples, ZnO@ZIF/C HNCs exhibit the highest ORR activity (remarkably close to Pt/C), both in terms of the onset potential ($E_{onset} = 0.92$ V) and the diffusion-limited current. Along with these findings, the standard Koutecky-Levich plots for the ZnO@ZIF/C HNCs (Figure 3.6(b and c)) from the rotational speed of rotating disk electrodes demonstrate a linear response with constant slopes over the potential range of 0.70–0.82 V. Hence, the slope plots (Figure 3.6(c)) are indicative of the electron transfer number (n), revealing a 4-electron ORR process pathway in the mixed (kinetic/diffusion) controlled region. This 4-electron pathway is thermodynamically more desirable in fuel cell applications as it elevates O_2 conversion and avoids the production of OH^- intermediates often created by the 2-electron pathway [17].

Also, the Tafel slope (Figure 3.6(d)) is crucial for understanding the reaction mechanism. For ZnO/C and ZnO@ZIF/C, the Tafel slopes calculated from linear sweep voltammetry (LSV) plots are 57 and 38.7 mV.dec⁻¹, respectively (Figure 3.6(d)). The ZnO@ZIF/C exhibits the highest ORR activity among the as-prepared porous carbon catalysts, and its lowest Tafel slope is lower than that of Pt/C standard (53.8 mV.dec⁻¹). All the results illustrated in Figure 3.6 show better ORR charge transfer kinetics for the laser-derived metal oxide/MOF@carbonous samples. Apart from the high ORR catalytic activity, the chronoamperometric test (Figure 3.6(e)) in O_2 -saturated 1 M KOH electrolyte solution exhibits outstanding long-term stability for the ZnO@ZIF/C HNC structures. Figure 3.6(e) presents a comparison between the normalized current density (%) at the relative half-wave potentials of the electrodes prepared with ZnO@ZIF/C and Pt/C samples. It is clear that even after thirty thousand cycles, the ORR current density of the ZnO@ZIF/C sample only degraded 7% compared to its initial value. However, the conventional Pt/C sample, under the same conditions, experienced a substantial decline in initial current density of around 23%, however. Interestingly, commercial Pt catalysts experienced a significant drop in initial current density of 21% within the first 1000 cycles, while LASiS-based HNCs show only a 5% drop in this initial stage (inset in Figure 3.6(e)). We attribute this phenomenon to the fact

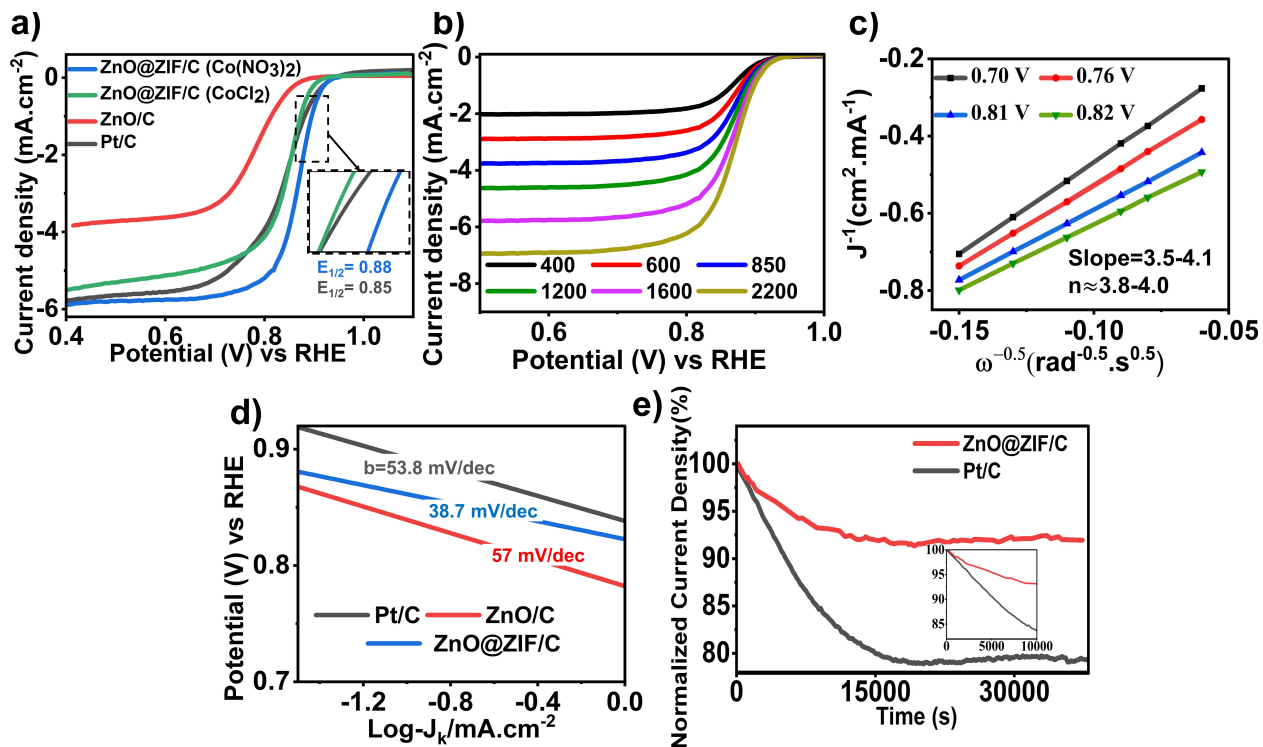


Figure 3.6: Electrochemical data for as-synthesized LASiS-derived HNCs and standard Pt/C; (a) Linear sweep voltammograms (LSV) in 1M KOH solution saturated with dissolved O₂ at 1600 rpm and a scan rate of 5 mVs⁻¹, (b) Rotating disk voltammograms (RDV) at various rotational speed, (c) Koutecky-Levich plots from RDE data for ZnO@ZIF/C in different potential ranges; (d) Tafel plots from (a); (e) Stability comparison for ZnO@ZIF/C and standard Pt/C *via* chronoamperometry.

that the transition metal/metal oxide@carbon matrix could create enhanced mechanical support and physical stabilization, resulting in significantly reduced mobility and higher electrochemical area due to lower surface contamination.

This study has paved the way for the rapid synthesis of novel nanomaterial as optimal ORR catalysts via a "green" synthesis method. The tandem LASiS-GRR approach, combined with post-pyrolysis, allows the engineering of better Pt- and PGM- free NMs that contain Co/ZIF-67@Zn/ZIF-8 bimetallic NPs with a unique morphology of ZIF-67 encapsulated by ZIF-8 structures. In addition, one can optimize the size, morphology, and overall structure of the two nano-porous Co/ZIF-67@Zn/ZIF-8 bi-MOFs synthesized using precisely the same "non-toxic" by simply changing the precursor metal salts during the synthesis process. To that end, after post-pyrolysis, the LASiS-synthesized MOF with membrane-shaped superstructures using a cobalt nitrate precursor exhibits superior ORR electrocatalytic activities even in harsh alkaline media. In summary, for the first time, a one-pot, reproducible, and green LASiS-GRR technique has been used for the facile and straightforward synthesis of ZnO/C and bimetallic ZnO@ZIF/C HNCs in metal oxide-MOF@carbonaceous support matrices with different morphologies that demonstrate electrocatalytic activities superior to costly high-performance commercial Pt-based electrocatalyst compositions under the extreme alkaline condition of a 1 M KOH solution.

The results of this study provide a broad range of possibilities for the rational design of MOF-based functional nanostructures using LASiS by selecting appropriate precursors and aqueous solutions.

Shifts in XRD peaks:

TGA experiments were employed to study the thermal decomposition of these MOFs during pyrolysis. Figure 3.9 depicts the TGA patterns of Zn/ZIF-8 and Co/ZIF-67@Zn/ZIF-8 at a scan rate of 10°C/min up to 700°C under N₂ atmosphere. The initial weight loss occurs due to solvent evaporation at ~170°C. The second weight loss for both MOF structures is related to the partial carbonization of organic residuals inside the pores of the MOFs. At higher temperatures (>400-500°C), the linker decomposes, leading to the partial collapse of the MOF structures; this also indicates the high thermal stability of the synthesized

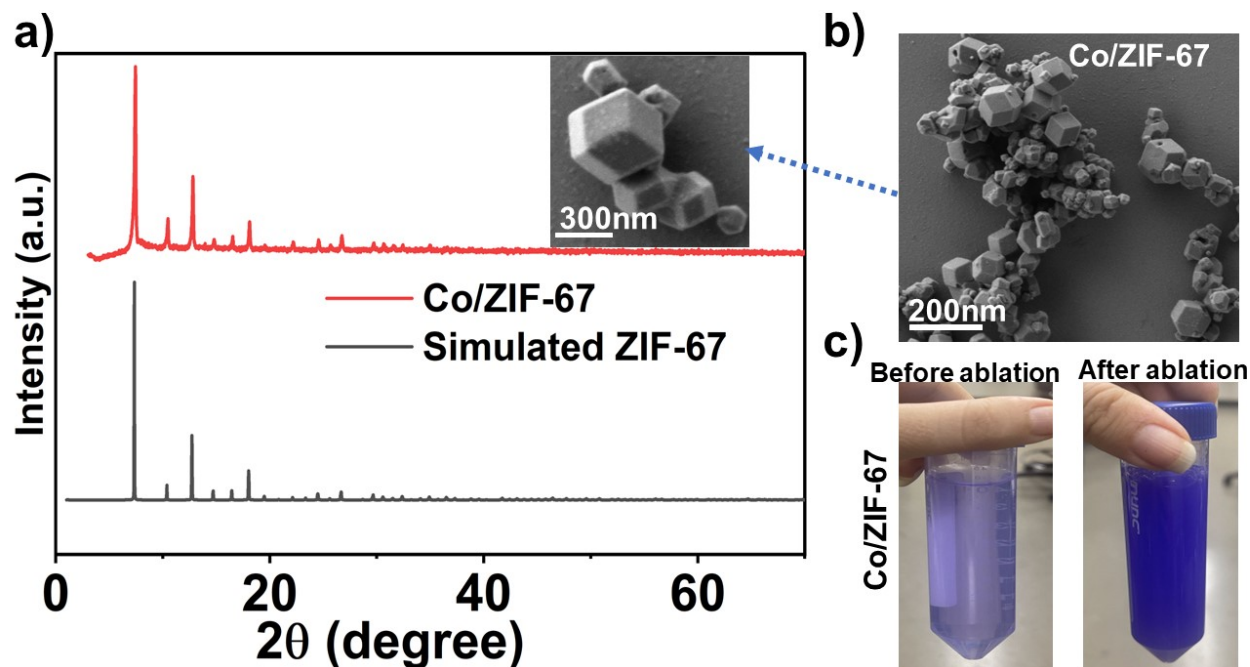


Figure 3.7: (a) XRD peaks $2\theta = 5-70$ (degree) highlighting the various crystal planes of Co/ZIF-67 compared to the simulated ZIF-67, (b) SEM micrographs of Co/ZIF-67 MOF, and (c) Visual evidence of Co/ZIF-67 formation.

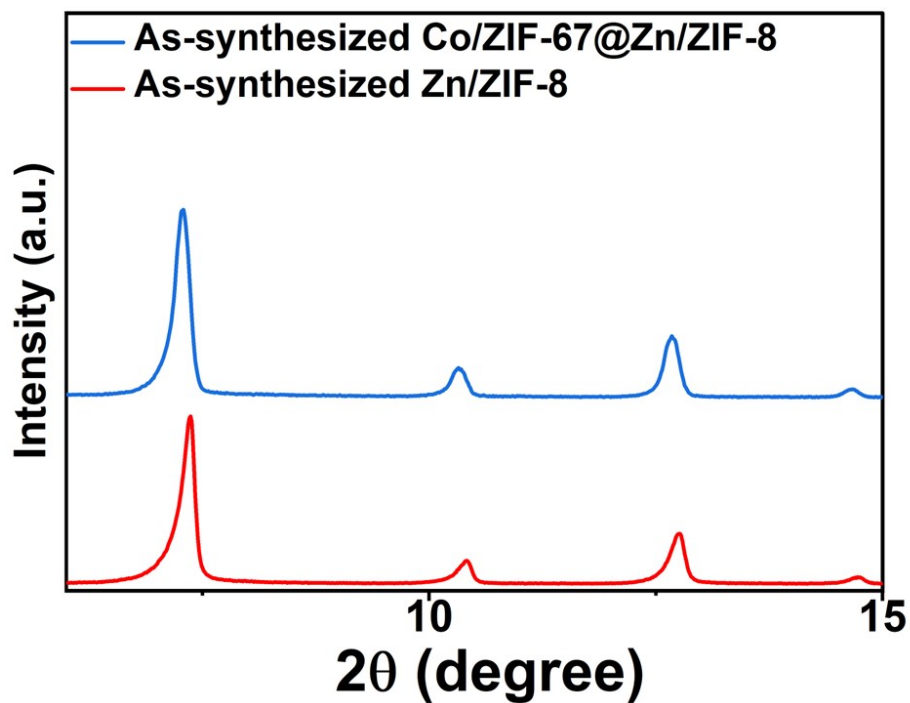


Figure 3.8: XRD data. A small shift to lower 2θ value could be related to the smaller pore sizes of Co/ZIF-67@Zn/ZIF-8 bi-MOF compared to Zn/ZIF-8 MOF sample.

ZIFs. The residual ~ 30 and 40 wt.% in each of the previously mentioned MOF structures correspond to the respective metal oxide formations. This finding is consistent with the post-pyrolysis XRD analysis (see Figure 3.4(a)).

One of the critical factors in MOFs is the pore size. Different pore sizes could affect the diffusion of reactants and products within the MOF structure, consequently influencing the overall ORR performance. MOFs with larger pores may allow for better accessibility of oxygen molecules, leading to enhanced catalytic activity. On the other hand, MOFs with smaller pores may exhibit higher selectivity toward specific ORR intermediates, thereby improving the overall efficiency. The surface area is another structural parameter that influences the efficacy of HNCs as electrocatalysts. MOFs with higher surface areas offer a larger active interface for the ORR process, facilitating a higher number of catalytic reactions and promoting efficient electron transfer. This characteristic can influence the overall ORR performance of MOFs. Furthermore, the coordination of the metal centers within the MOF structure plays a role in the efficacy of the material as an electrocatalyst, namely, the coordination geometry and ligand environment around the metal centers can dictate their catalytic activity and selectivity in the ORR. By modifying the metal centers, we tuned the catalytic properties of bi-MOFs and optimized their ORR performance. Additionally, the role of active sites within the MOF structure and their interaction with oxygen molecules during the ORR process is critical. Active sites, such as metal centers or defect sites, can facilitate the adsorption and activation of oxygen molecules, leading to efficient ORR kinetics. To that end, our study elucidates the intricate relationship between the MOF structures and their respective catalytic performance. By investigating parameters such as pore size, surface area, metal center coordination, and active sites, we have paved the way for a fundamental understanding of structure/morphology and catalytic activity and efficiency of these MOFs and bi-MOFs as ORR for various electrochemical [137, 56]

Compared with traditional wet chemical routes, laser ablation in solution synthesis possesses a host of desirable features, including the following:

Direct and Rapid Nanoparticle (NP) Formation: Laser ablation in solution synthesis involves the use of a high-energy laser to ablate a target metal immersed in a

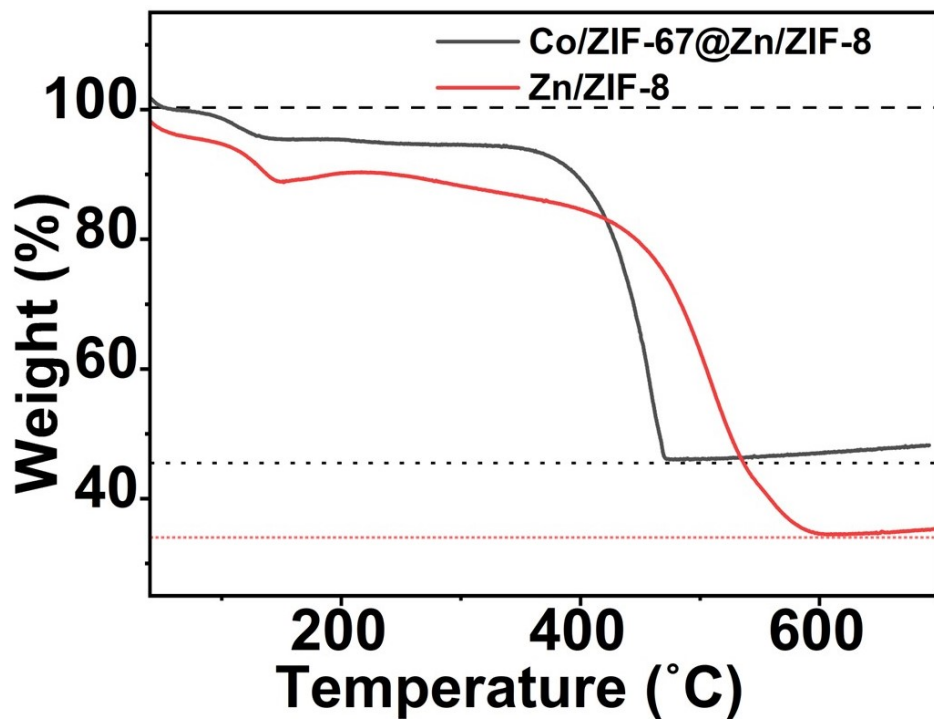


Figure 3.9: Thermal decomposition of LASiS-GRR synthesized Co/ZIF-67@Zn/ZIF-8 (red) and Zn/ZIF-8 (black) *via* TGA.

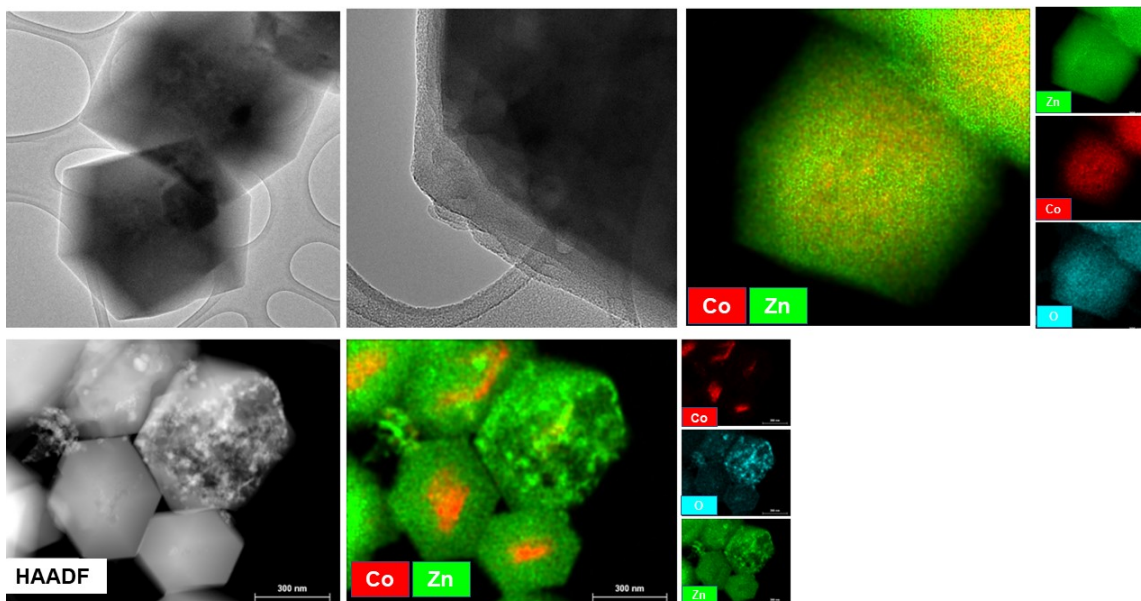


Figure 3.10: STEM and elemental mapping micrographs of Co/ZIF-67@Zn/ZIF-8 bi-MOF before (top) and after (bottom) pyrolysis.

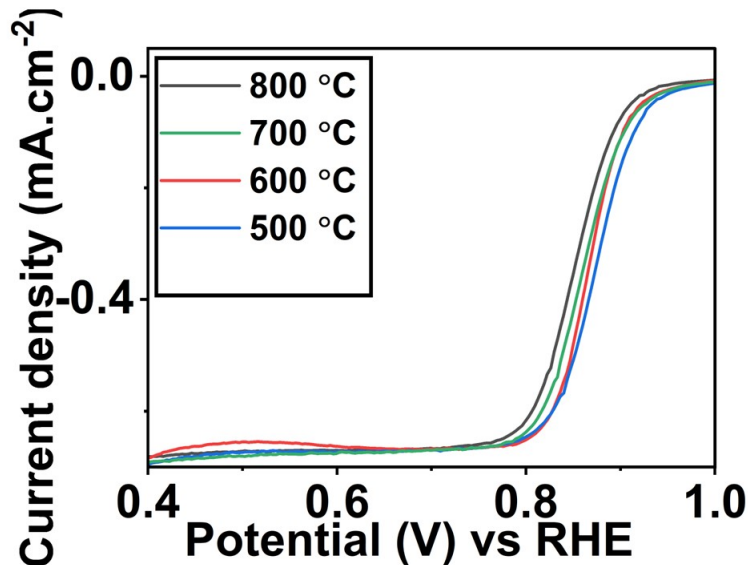


Figure 3.11: Effect of different pyrolysis temperature on electrochemical data for as-synthesized LASiS-GRR derived NCs; ORR analysis *via* linear sweep voltammograms (LSV) in 1M KOH solution saturated with dissolved O₂ at 1600 rpm and a scan rate of 5 mV/s.

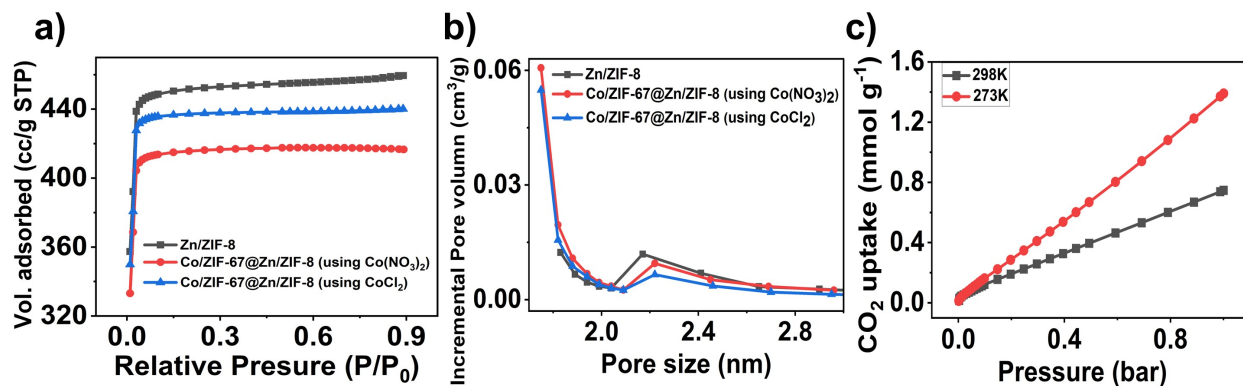


Figure 3.12: (a) Adsorption isotherm of hydrogen on, (b) Pore size volume of ZIF and bi-ZIFs, and (c) CO₂ uptake isotherms being collected at 273 and 298K of Co/ZIF-67@Zn/ZIF-8 using Co(NO₃)₂·6H₂O.

Table 3.1: The Physical properties of BET surface area, pore size, pore volume of MOFs and bi-MOFs. N₂ adsorption volume at P/P₀ = 0.8.

Sample	BET SA	Micropore Volume	Micropore Area
ZN/ZIF-8	1521 .47	0.067	1459.30
Co/ZIF-67@Zn/ZIF-8 (<i>CoCl</i> ₂)	1470.94	0.662	1438.58
Co/ZIF-67@ZN/ZIF-8 (<i>Co(NO</i> ₃) ₂)	1399.22	0.624	1356.20

liquid medium. This process enables the direct and rapid formation of NPs in solution without the need for complex chemical reactions, surfactants, or precursors.

Solvent Flexibility: Laser ablation in solution makes use of various types of solvents or liquid media loaded with various precursors for secondary chemical reactions driven by the rate-controlled ablation of the primary metal target, which produces the seeding NPs. This provides the flexibility in choosing a suitable environment for NP synthesis while allowing for a suitable design of experiments to synthesize complex multi-elemental NPs through the selection of solution-phase precursors for secondary chemical reactions with the seeding NPs.

Size and Shape Control: By adjusting laser parameters such as energy, fluence, and pulse duration, laser ablation in solution offers control over the sizes and shapes of the as-synthesized NPs. This tunability allows the production of NPs with specific dimensions, leading to tailored properties and enhanced functionality.

High Purity and Mono-dispersity: Laser ablation in solution typically result in high-purity NP synthesis. The ablation process directly converts the target material into NPs, minimizing the presence of impurities or by-products from harsh chemical reagents or surfactants. Additionally, rapid cooling of the ablated NPs in the liquid medium promotes monodispersity, yielding NPs with a narrow size distribution.

Surface Modification and Functionalization: Laser ablation in solution allow for in situ surface modification and functionalization of synthesized NPs. It is possible to introduce suitable ligands or precursors into the liquid medium during the synthesis process. This provides the ability to tailor the NP surfaces with the desired functionalities, improving their stability, dispersibility, or compatibility for specific applications.

The choice between LASiS and wet chemical routes depends on the specific requirements of the application and the desired properties of the nanoparticles. Both methods have their own advantages and limitations. For a given application, consideration of critical factors, including target material, particle size control, scalability, purity requirements, and the need for surface modification, is critical in selecting the desired synthesis process. The advantages mentioned above make laser ablation synthesis particularly suitable for a host of applications, including the one discussed in this study.

3.7 summary

This study has paved the way for the rapid synthesis of novel nano catalysts as optimal catalysts with desired structural properties and functionalities for ORR in AEMFCs through a completely "green" synthesis method. The tandem LASiS-GRR approach, combined with post-pyrolysis treatments, allows the engineering of better Pt- and PGM-free NMs that contain Co/ZIF-67@Zn/ZIF-8 bimetallic NPs with a unique morphology of ZIF-67 encapsulated by ZIF-8 structures. In addition, one can optimize the size, morphology, and overall structure of the two nano-porous Co/ZIF-67@Zn/ZIF-8 bi-MOFs synthesized using precisely the same "non-toxic" by simply changing the precursor metal salts during the synthesis process. To that end, after post-pyrolysis, the LASiS-synthesized MOF with membrane-shaped superstructures using a cobalt nitrate precursor exhibits superior ORR electrocatalytic activities even in harsh alkaline media. In summary, for the first time, a one-pot, reproducible, and green LASiS-GRR technique has been used for the facile and straightforward synthesis of ZnO/C and bimetallic ZnO@ZIF/C HNCs in metal oxide-MOF@carbonaceous support matrices with different morphologies that demonstrate electrocatalytic activities superior to costly high-performance commercial Pt-based electrocatalyst compositions under the extreme alkaline condition of a 1 M KOH solution. The results of this study provide a broad range of possibilities for the rational design of MOF-based functional nanostructures using LASiS by selecting appropriate precursors and aqueous solutions.

Chapter 4

Introduction to Additive Manufacturing of Laser-Induced ZnCo-Based Metal-Organic Framework Composited with Reduced Graphene Oxide

Supercapacitors (SCs) have the unique ability to rapidly recharge while providing substantial power output. This characteristic bridges the gap between conventional capacitors and batteries, making them an indispensable component in energy storage applications. In the world of SC technology, metal-organic frameworks (MOFs), due to their high porosity, tunable pore size distribution, ease of synthesis, and exceptional structural adaptability are emerging as promising electrode materials. When MOFs are composited with various materials, including carbon-based compounds and graphene, they can achieve the required conductivity and chemical stability for high-performance electrode materials in SCs. This study presents a facile and cost-effective method, called laser ablation synthesis in solution (LASiS), for the synthesis of bimetallic MOFs composited with reduced graphene oxide (rGO), namely, ZnCo bi-MOF-rGO hybrid nanocomposite (HNC). Specifically, we report

the results of a comprehensive examination of morphological, and structural analyses, as well as electrochemical properties of LASiS synthesized ZnCo bi-MOF-rGO HNCs. These experiments demonstrated that ZnCo bi-MOF-rGO exhibits a high specific capacitance of 1092 F/g at 1.0 A/g in a 0.5 M Na₂SO₄ electrolyte. In addition, we have successfully integrated these bi-MOF-rGO HNCs with suitable solvents, viscosity modifiers, in-house synthesized porous carbon (PC), commercial graphene, and binders into an active layer ink material for the fabrication of high-performance SCs *via* sequential inkjet printing. Moreover, we elucidate the dependence of the final properties of the printed SCs on printing parameters and the structure and composition of the HNCs. Rational optimization of the previously mentioned parameters has enabled us to achieve remarkable electrochemical performance in our printed ZnCo bi-MOF-rGO electrodes, *i.e.*, the specific capacitance of 670 F/g at 2.0 A/g. To that end, we have paved the way for the incorporation of this class of material into energy storage applications, particularly in the fabrication of high-performance printed electronics using laser-induced material.

4.1 Introduction

The escalating global concerns associated with current energy demands have driven researchers to explore alternative technologies for energy conversion and storage systems. Electrochemical energy storage devices, particularly supercapacitors (SCs), have gained significant attention due to their high-power delivery and long cycle life.[126, 86] While SCs excel in high power delivery and long cycle life, they generally offer moderate to low energy density compared to traditional batteries.[99] The development of next-generation SCs requires the realization of both high-energy and high-power density, making them ideal for applications in various energy-related devices, including hybrid electric vehicles, portable power supplies, and electronic devices.[7] In terms of energy density, the electrochemical energy storage capacity of SCs is significantly influenced by their electrode materials.[40] Among the range of active electrode materials, including carbon, metal oxides, conducting polymers, and other compositions, graphene has emerged as an exceptionally promising candidate for energy storage applications.[33] However, SCs composed of exclusively of

graphene-based electrodes show a low specific capacitance, [11] therefore, composites consisting of metal nanoparticles interfaced with graphene have been developed as electrode materials to enhance the performance of modern SC systems [54] owing to their high surface area, electrical conductivity, and mechanical properties.[102]

Metal-organic frameworks (MOFs), on the other hand, have recently found diverse applications in gas storage[84], catalysis[104], biosensors[49] and solar cells[46]. MOFs possess unique characteristics such as high specific surface area, hierarchical pore size distribution, reconfigurable structure, and excellent chemical and thermal stability.[37, 9] In the domain of SCs, various MOFs have shown promise as potential electrode materials due to their highly porous structures.[26] However, pristine MOFs typically suffer from poor electrical conductivity, which does not allow for efficient charge transfer to the current collector.[44] To address this limitation hybrid nanocomposites that combine MOFs with conductive materials such as conducting polymers, reduced graphene oxide, and graphene have been developed.[76] These electrically conductive composites offer a high surface area, in comparison to other electrode materials such as pristine graphene, graphene oxide, and carbon materials such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs). To date, most studies have focused on SCs comprised of different MOF composites and aqueous electrolytes. However, detailed studies of electrode assembly through additive manufacturing and the resulting device performance remain an active research area. The electrode material characteristics and electrolyte choice significantly impact the specific capacitance, cyclic stability, energy, and power density of MOF-based SCs. To that end, three-dimensional (3D) printing technology has proven effective in the construction of 3D devices comprised of MOF-based materials characterized by low density, high porosity, and adjustable electrical conductivity. Specifically, these devices facilitate the diffusion of electrolyte ions, thus enhancing the electrochemical performance of electrode materials.[134]

This study presents a simple yet elegant technique, laser ablation synthesis in solution (LASiS), for the fast and environmentally friendly synthesis of a porous composite material consisting of ZnCo-based bi-MOFs-rGO. We selected reduced graphene oxide (rGO) as it is a cost-effective alternative to graphene.[101] We chose LASiS for material synthesis due to its advantages in facilitating precise control over the synthesis process. Unlike conventional

nanofabrication techniques, LASiS does not require precise control of synthesis parameters such as pressure and temperature, and it is a fast and facile technique that is environmentally friendly and cost-effective for nanomaterial fabrication. Our previous publications contain a more in-depth discussion of the physicochemical processes involved during LASiS. [104, 87, 54, 86]

Synthesizing and combining ZnCo bi-MOFs with rGO during LASiS yields a highly porous and electrically conductive hybrid composite with improved electron transport and electrolyte ion diffusion properties compared to bare MOFs. A key component of the superior charge transfer of our hybrid composite is the presence of amide linkages in ZnCo bi-MOFs-rGO that facilitate the formation of a π -conjugated structure. In addition, nitrogen-doped graphene oxide, formed during LASiS by using imidazole in the GO solution, contributes to modifying the electronic properties of the in-situ synthesized MOF and bi-MOF on rGO-based HNCs. To this end, we investigated the specific capacitance, energy density, and cyclic stability of ZnCo bi-MOF-rGO HNCs as an SC electrode material in 0.5 M Na₂SO₄. Our studies reveal that the ZnCo bi-MOF-rGO system exhibits high specific capacitance, energy density, and excellent cyclic stability. Furthermore, we use sequential additive manufacturing to 3D print SC devices using ZnCo bi-MOF-rGO, Co MOF-rGO, and Zn-MOF-rGO electrodes. The printed ZnCo bi-MOF-rGO SC demonstrates improved specific capacitance and energy density compared to those of previously reported MOF-based devices. To the best of our knowledge, this is the first report to highlight the excellent supercapacitor performance of an inkjet-printed MOF-rGO HNC electrode system. Finally, detailed studies of bi-MOF-rGO composites showed prominent $\pi - \pi$ interactions, which enable layer-by-layer molecular arrangement. We postulate that the $\pi - \pi$ interactions enhance interfacial charge transfer processes and in turn increase the energy densities of these electrochemical SC devices. Furthermore, the study introduces a versatile solution to accommodate both pseudocapacitance and double layer capacitance by using a ZnCo bi-MOF composited with rGO in combination with different allotropes of carbon, allowing for efficient energy storage.

4.2 Experimental Section

This section provides an overview of the methods and materials utilized to (1) synthesize the LASiS-derived MOF and bi-MOF-rGO HNCs, and (2) prepare and assemble the 3D-printed SC device from the engineered HNCs.

4.2.1 Synthesis of ZnCo Bimetallic MOF-rGO Heterostructures *via* LASiS-GRR

Our previous publications provide a detailed description of the Laser Ablation Synthesis in Solution-Galvanic Replacement Reaction (LASiS-GRR).[104, 87, 54, 86, 103] Specifically, the process initiates with the laser ablation of a metal target submerged in a liquid solution. This action triggers the formation of a laser-induced plasma plume at the interface between the solid target and the liquid medium. The resulting high-temperature and pressure conditions within the plasma create a unique environment, facilitating the occurrence of out-of-equilibrium chemical reactions. Such conditions allow synthesis of unique materials by combining the liquid phase and target elements in a thermodynamically metastable state. Post-ablation, the plasma gradually cools down and depressurizes, which in turn leads to the growth of clusters, resulting in the formation of the desired nanoparticles (NPs) and nanocrystals. We use LASiS due to its successful application in our previous publications that highlight its efficacy in achieving desired material characteristics.

In this study, we employed LASiS-GRR, to efficiently synthesize bimetallic heterostructures of ZnCo MOFs-rGo HNCs. These HNCs serve as active electrode material for high-performance energy storage devices. We sourced the necessary starting materials from Sigma-Aldrich and Kurt J. Lesker. We used Zinc (Zn) and Cobalt (Co) pellets with a purity of 99.5% and dimensions of 1/4" in diameter and 1/4" in height as metal targets during LASiS. A solution containing in-house synthesized GO suspensions in deionized (DI) water with a concentration of 20 mg L⁻¹ was bath sonicated for approximately 60 minutes. To achieve the desired pH level (pH = 13), we added potassium hydroxylate (KOH, > 99%) to the solution. Two Cobalt (II) solutions, namely Cobalt (II) nitrite (Co(NO₃)₂.6H₂O) and Cobalt(II) chloride (CoCl₂.6H₂O) at concentrations of 11 mg/L, were prepared by dissolving

specific quantities of the respective precursor salts in 35 mL of potassium hydroxide and GO solution. We added 1.7 g of 2-methylimidazole (Hmim) to each solution batch and in turn we transferred it to the LASiS reactor cell. Subsequently, we placed a Zn pellet on a holder at the bottom of the reactor cell and pulsed Nd-YAG laser ablation (1064 nm) with a pulse energy of 310 mJ/pulse and a repetition rate of 10 Hz ablated the metal target for 10 minutes to produce ZnCo biMOFs-GO HNCs. We centrifuged the LASiS-synthesized at 4700 rpm for 20 minutes, and we collected the precipitate portion of each sample. To remove all unreacted chemical precursors, we washed the collected materials with DI water, followed by three methanol washes. We synthesized Zn and Co MOFs-GO samples using the same solution and by ablating the Zn and Co targets, respectively, but without using any precursor salts. To synthesize ZnCo bi-MOF-rGO, Zn and Co MOFs-rGO HNCs, we dried the final product of ZnCo bi-MOF-GO, Zn and Co MOFs-GO for 24 hours in a vacuum. This step included vacuum heating at 250°C for 3 hours. Figure 4.1(a) depicts the schematic of the synthesis process.

Structural, Compositional, and Morphological Characterization

Different techniques were employed to analyze the structure and composition of the synthesized material. We performed X-ray diffraction (XRD) analysis on a Phillips X’Pert-Pro diffractometer with a Cu K α monochromatized radiation source ($\lambda = 0.1541$ nm), operated at 45 kV and 40 mA. A Nicolet iS50 FTIR spectrometer with an absorption spectra range of 5000-400 cm⁻¹ was used to attain the Fourier transform infrared spectroscopy (FTIR) spectra. Microscopy and elemental mapping were performed using a Philips XL-30ESEM scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX) spectroscopy to acquire SEM-EDS micrographs. Transmission Electron Microscopy (TEM) analysis and elemental mapping-EDX were conducted on a JEOL JEM 1400-Flash, and a Thermofisher Tecnai Osiris scanning/transmission electron microscope (S/TEM) operated at an accelerating voltage of 120 kV. Raman spectra was obtained using an NT-MDT NTEGRA spectra instrument equipped with a 532 nm green laser beam. Finally, we conducted thermogravimetric analysis (TGA) in an inert N₂ environment using a standard TA instrument (Q50 15GA). The samples were heated from ambient temperature to 900

°C at a rate of 10 °C/min. These comprehensive characterization techniques collectively confirm the successful preparation of novel LASiS-synthesized bi-MOF-rGO HNCs as a high-performance supercapacitor electrode material.

Electrochemical Characterization

We used a conventional electrochemical cell (EC) manufactured by Pine Instruments LLC for the electrochemical experiments. The device has a saturated double-junction Ag/AgCl reference electrode and a platinum (Pt) counter electrode. All electrochemical characterizations of the LASiS-derived HNCs were conducted with this three-electrode configuration. Furthermore, when the electrodes of the printed device were characterized, we employed a two-electrode configuration, and experiments were carried out using a research-grade SP-150 biologic potentiostat. To assess the supercapacitance properties of LASiS-synthesized HNCs, we fabricated an in-house working electrode. Initially, we prepared a slurry mixture by vigorously stirring a combination of 80% LASiS HNCs, 10% in-house synthesized porous carbon (PC), and 10% polyvinylidene difluoride (PVDF, Aldrich) binder. Subsequently, we drop-cast approximately 6-10 mg of the resulting slurry onto a highly porous squared-shaped nickel (Ni) foam (1 cm²). The loaded Ni foam substrate was later dried under vacuum conditions at 80°C for 8 hours and then pressed at 10 MPa for 5 seconds to obtain the maximum surface area for the working electrodes. We used a supporting electrolyte of 0.5 M Na₂SO₄ (pH 7.2) to enhance the electrolyte conductivity. For comparison, the same ink containing commercial PC was also formulated. For the cyclic voltammetry (CV) tests, we operated within a fixed potential range of -0.30 to 0.70 V at a scan rate of 20 mV/s. Cyclic charge-discharge (CD) tests were carried out at a current density of 1.0 A/g over a potential range from -0.3 to 0.7 V. The specific capacitance (C) is calculated from the CD curves using the following equation:

$$C = \frac{I_m \times \Delta t}{\Delta V} (Fg^{-1}) \quad (4.1)$$

That C (F / g) represents the specific capacitance, $I_m = \frac{I}{m}$ (A/g) denotes the current density (current per unit mass) during discharge, m (g) is the weight of the electroactive material, and ΔV (V) is the potential drop.

4.2.2 Preparation and Assembly of Printed Supercapacitor (SC) Device

Printed SCs allow rapid prototyping of 3D electrode architectures that, in turn, can be used for optimizing the device performance. The 3D printed electrodes composed of porous MOF-rGO HNCs and PC offer high porosity and a large specific surface area, *i.e.*, enhanced contact area between the electrodes and the electrolyte, boosting electrochemical performance. Furthermore, producing the entire SC device via 3D printing can reduce manufacturing costs and complexity while increasing flexibility and production capacity.

In our design, a conductive silver (Ag) nanoparticle paste, with a resistivity of $1.59 \mu\Omega\cdot\text{cm}$ at 20°C serves as the current collector layer in the printed design, as schematically shown in Figure 4.2(a). The Ag layer is printed and annealed at 120°C . The active layer of the pseudocapacitor comprises of MOFs and bi-MOFs-rGO added to carbon-based electroactive materials interfaced with high purity electronic grade graphene nanoflakes from MSE supplies ($> 98\%$ purity), 50:50 mixture of PC and CNFs, ethylcellulose (E-C) and terpineol from Sigma-Aldrich. To ensure effective charge transport through a percolated conductive network, graphene nanoflakes (0.90 g), PC (0.05 g), and CNF (0.05 g) are added to MOF and bi-MOF-rGO HNC made with LASiS (0.20 g). Subsequently, the respective active layers are dispersed in 45 mL of methanol. The solution is bath sonicated for 60 minutes, followed by the evaporation of methanol at 40°C under vacuum conditions for 24 hours. The resulting powder is then dispersed in 4 mL of terpineol by manual stirring. Finally, 0.5 g of E-C is added to the powder and terpineol solution and stirred manually for five to ten minutes to obtain the desired consistency. The gel polymer electrolyte (GPE) layer are prepared by dissolving polyvinylidene difluoride (PVDF) and lithium perchlorate (LiClO_4 , 0.25 M, PVDF: $\text{LiClO}_4 = 2:1$) in propylene carbonate at 140°C following 60 minutes of continuous stirring. After the GPE layer solution transforms into a viscous gel

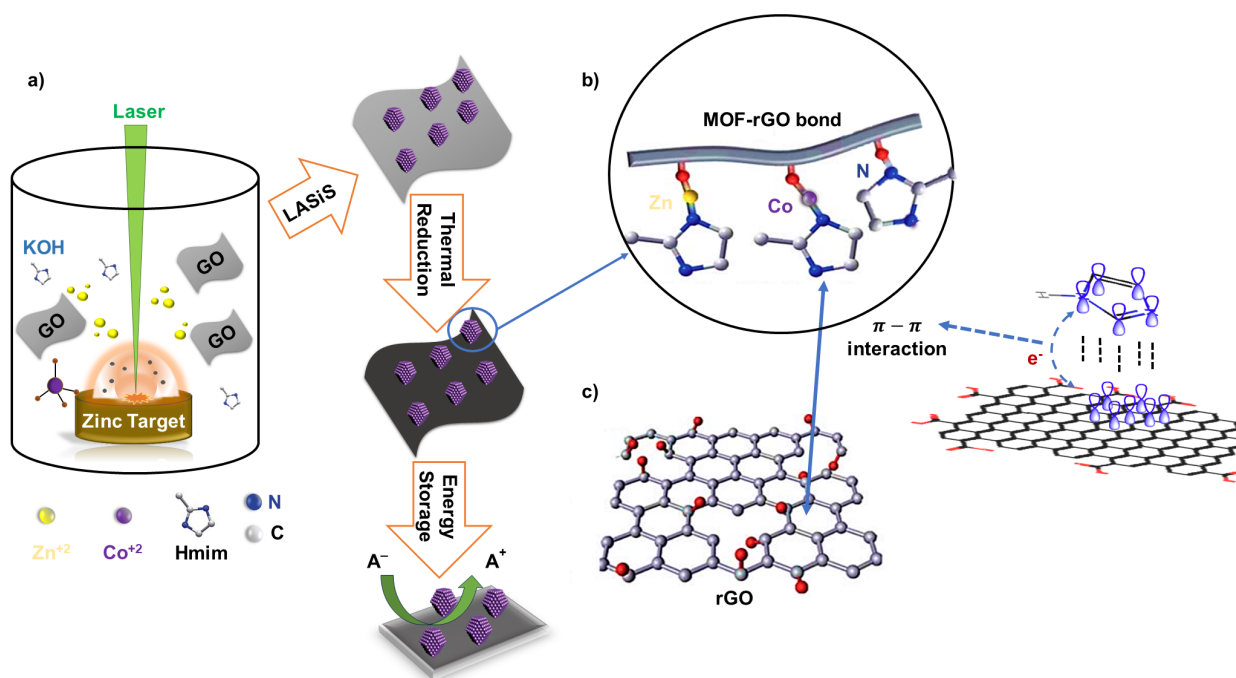


Figure 4.1: (a) Schematic illustration of LASiS methodology used to synthesize bimetallic ZnCo bi-MOF-derived SC material, (b) Coordination bonds between reduced rGO and ZnCo bi-MOF, (c) Crystalline structure of reduced Graphene Oxide.

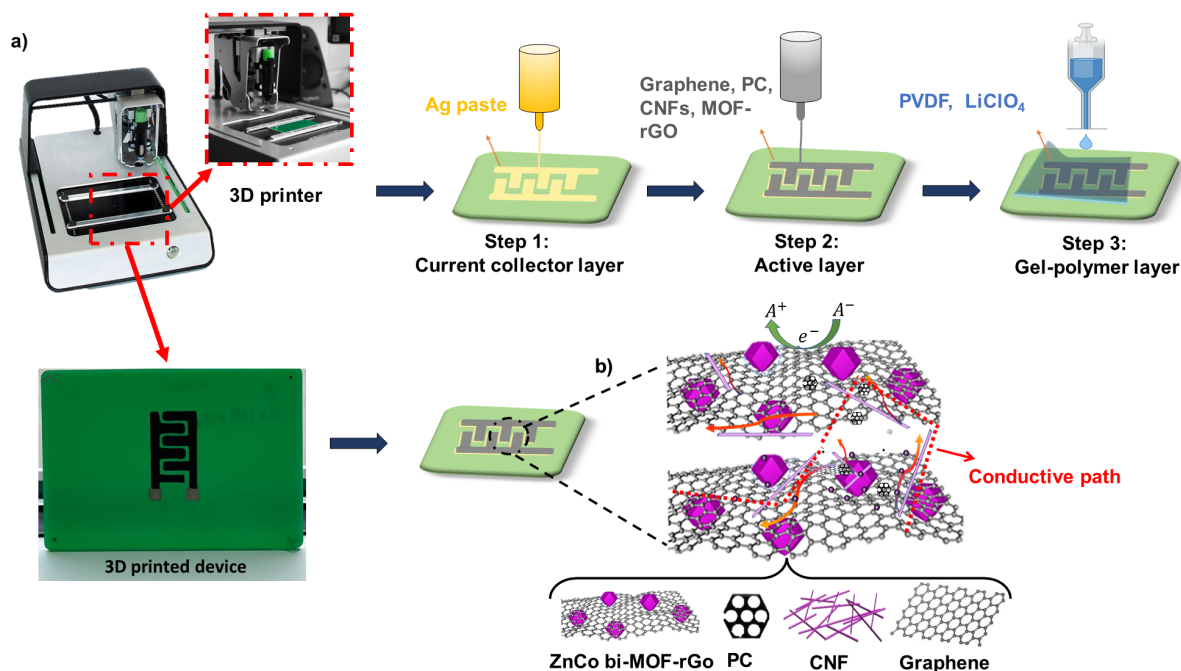


Figure 4.2: Schematic illustrations of (a) sequential layer-on-layer procedure for the 3D printing of SC electrodes; (b) percolated conductive network of PC, CNFs, MOF-rGO, and graphene nanosheets.

upon cooling, it is printed on the active layer. The synthesis process of porous carbons can be found in supporting information (SI).

Printing process

The device patterns were created through a sequential 3D printing process, where each layer was printed at a time, as schematically shown in Figure 4.2 (a). The printing patterns for the active and current collector layers were initially designed using EAGLE / Fusion 360 Software and then transformed into Gerber format (GBR). These patterns consisted of interdigitated layouts for the current collector and the active layer, consisting of six lines with three lines for the positive and three for the negative electrodes. The size and shape of these patterns can be customized to meet the specific requirements of the printing process. Sequential layer-on-layer printing was used to assemble the final printed SC design. The active and current collector layers were printed using a Voltera printer (V-One, a desktop PCB printer). The GPE layer was printed using an Engine HR printer (Model: Hydra 16A printer of the Hyrel 3D EHR system). The silver (Ag) paste layer was printed onto the PCB substrate based on the aforesaid Greber pattern. With its high conductivity, the Ag current collector facilitates rapid charge transfer from the active layer. The active layer was prepared by dispersing the desired HNCs into a previously prepared paste containing graphene, PC, CNFs, and E-C. This active layer was printed on top of the Ag layer and subjected to thermal treatment at 80°C. Finally, the GPE layer was printed on top of the active layer and allowed to dry at room temperature overnight.

4.3 Results and discussion

In what follows, we present a comprehensive characterization of the successful LASiS-driven synthesis of ZnCo bi-MOF-rGO structures. In turn, we provide a summary of the materials and their electrochemical properties, highlighting their unique features and performance. In the following sections, we discuss how LASiS derived HNCs and additive manufacturing is used to construct a 3D-printed SC device. Subsequently, we discuss the supercapacitive properties of these printed SC devices.

4.3.1 LASiS synthesized ZnCo biMOF-rGO HNCs

Structural and morphological characterizations

We characterized the morphology and composition of the synthesized MOFs and bi-MOFs synthesized directly on GO by SEM, TEM, and elemental mapping of the laser-driven material. The results shown in Figure 4.3 indicate that Co, Zn MOF-GO HNCs, and ZnCo bi-MOFs-GO, synthesized using CoCl_2 and $\text{Co}(\text{NO}_3)_2$ precursors, contain a distinctive layered cubic or membrane-shaped nanostructure embedded on top of GO nanosheets. In particular, in this configuration GO serves as a two-dimensional (2D) substrate in the layered structure. Figure 4.3(e to h) shows that the MOFs are coated with flaked or rolled GO and integrated into an interconnected GO framework structure while preserving the distinct attributes of the MOFs and GO. This figure provides a magnified SEM micrograph of a Cubic MOF structure covered with GO. These LASiS-synthesized GO-covered MOFs and bi-MOFs on GO sheets can provide a practical yet effective platform for energy storage applications. STEM, and elemental mapping of LASiS-derived MOFs synthesized without using GO during LASiS are shown in Figure 4.4.

Furthermore, the successful integration of bi-MOFs in GO sheets was validated using TEM and elemental mapping images, as presented in Figures 4.3 (e-h) and 4.4. These results provide compelling evidence of the MOF distribution across the GO sheets, accompanied by the rolling of the GO sheets, which may be influenced by external factors. It is difficult to neglect that the embedding of the MOF on GO sheets during LASiS could result in rolling and flaking of GO sheets due to the presence of π - π stacking, which increases the likelihood of generating π -conjugated structures. Elemental mapping images in Figure 4.4, additionally provide a visual representation of the spatial distribution of Zn and Co cations within the MOF structure, providing evidence of the fabrication of bimetallic MOFs. Upon close inspection of Figure 4.4, it becomes evident that N-doped GO also plays a vital role in preventing formation of a core-shell structure in bi-MOFs. This results in a higher concentration of metallic sites on the surface, which could, in turn, enhance the capacitance. Specifically, the presence of Co cations on the surface of the LASiS synthesized bi-MOFs-rGO contributes to enhanced capacitance.

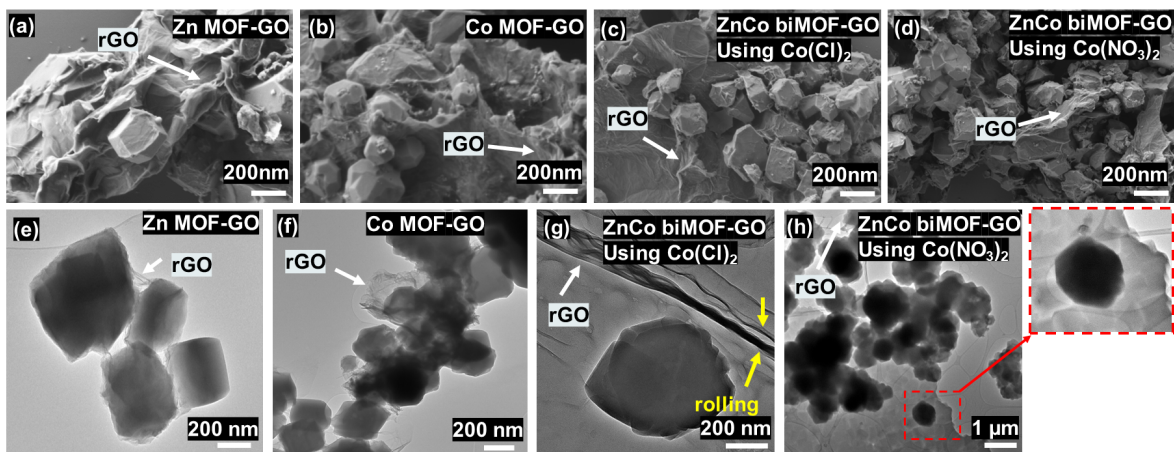


Figure 4.3: SEM micrographs of (a) Zn MOF on GO, (b) Co MOF on GO, (c) ZnCo biMOF on GO using CoCl_2 precursor salt, and (d) ZnCo biMOF on GO using $\text{Co}(\text{NO}_3)_2$ precursor salt; TEM Micrographs of (a) Zn MOF on GO, (b) Co MOF on GO, (c) ZnCo biMOF on GO using CoCl_2 precursor salt, and (d) ZnCo biMOF on GO using $\text{Co}(\text{NO}_3)_2$ precursor salt

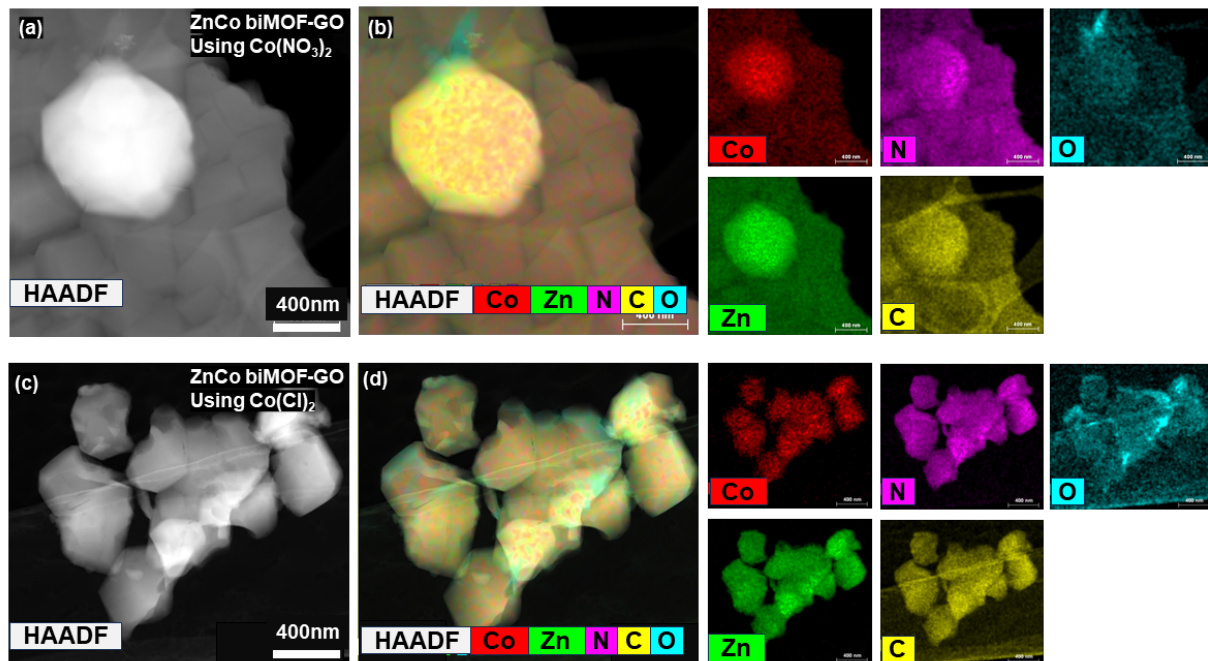


Figure 4.4: SEM micrographs of (a and b) STEM and elemental mapping micrographs of ZnCo biMOF on GO using $\text{Co}(\text{NO}_3)_2$ precursor salt; STEM and elemental mapping micrographs of (c and d) ZnCo biMOF on GO using CoCl_2 precursor salt.

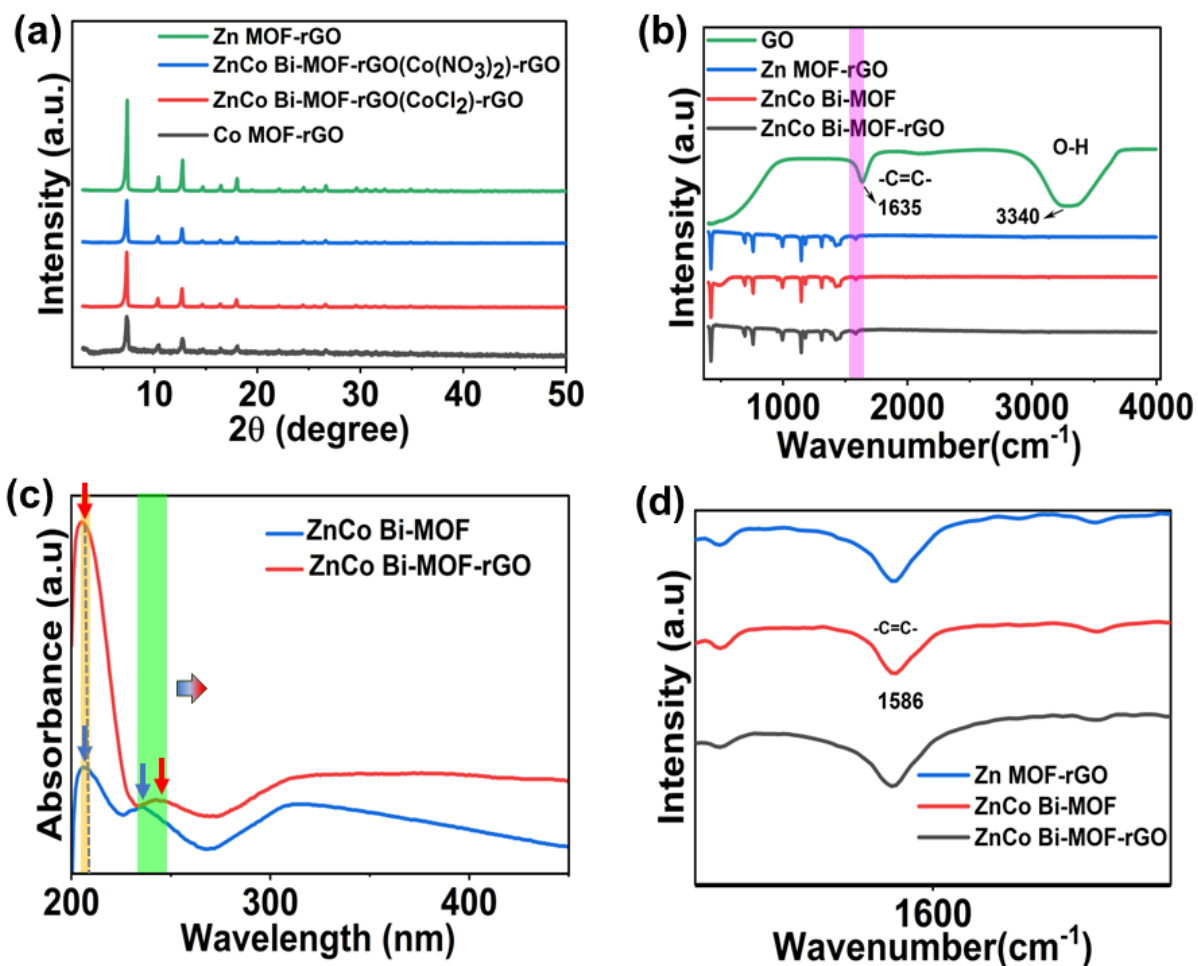


Figure 4.5: (a) XRD peaks $2\theta = 5 - 50$ (degrees) highlighting various crystal planes of Zn MOF-rGO, ZnCo biMOF-rGO using Co(NO₃)₂ and CoCl₂ precursor salts, (b) FTIR spectrum within 400–4000 cm⁻¹ depicting various functional groups in GO, Zn MOF-rGO, ZnCo biMOF-rGO, and ZnCo biMOF structures, (c) UV-vis absorbance spectra of ZnCo biMOF-rGO and ZnCo biMOF, (d) Magnified FTIR spectra to elaborate the -C=C- bonding in different samples

In what follows, we discuss the results of our detailed structural characterizations of the previously mentioned MOF/bi-MOF-rGO samples, focusing on XRD analyses (see Figure 5 (a)) for Zn and Co MOF-rGO and ZnCo bi-MOF-rGO using two different precursor salts, namely, $\text{Co}(\text{NO}_3)_2$ and CoCl_2 . To that end, the presence of sharp and distinctive peaks in the LASiS-synthesized MOFs-rGO and bi-MOF-rGO samples that closely match the simulated diffraction patterns of Zn and Co MOFs [73], confirms the existence of highly crystalline MOF phases. Figure 5(a) reveals the presence of XRD peaks attributed to the MOFs and biMOF-rGO crystals. However, presence of a slight shift to lower 2θ values in the XRD peaks suggest smaller pore sizes of ZnCo bi-MOF-rGO compared to Zn and Co MOF-rGO samples, validated by Brunauer-Emmett-Teller (BET) surface area analysis (See Figure 4.6). In addition, FTIR measurements identify the effective surface-specific functional groups present in these LASiS-synthesized MOF and bi-MOF-rGO HNCs. Figure 4.5(b) depicts the spectral features of the Zn MOF-rGO and the ZnCo bi-MOF-rGO compared to GO and the ZnCo bi-MOF. The spectral bands of 756 cm^{-1} are due to the 2-Methylimidazole (Hmim) out-of-plane bending ring, while the stretching at 1424 cm^{-1} is due to the in-plane bending [2]. Strong C-N vibrations at 1310 cm^{-1} , and C = N peaks at 1594 cm^{-1} [87]. Strong C-N vibrations at 1310 cm^{-1} and the C=N vibration at 1594 cm^{-1} indicate the presence of Hmim as a linker in the MOF structure. In general, the peak at $1250\text{-}1020\text{ cm}^{-1}$ is indicative of C-N stretching, and at $1650\text{-}1580\text{ cm}^{-1}$ is a signature of N-H vibrations in the same structure or due to N-H bending in the Hmim molecule. Furthermore, the stretch of the aromatic ring in the imidazole structure is responsible for the weak peak at 1630 cm^{-1} . The strong metal linker bond, such as Co-N or Zn-N at 434 cm^{-1} confirms the presence of metal centers in MOF and MOF/biMOF-rGO HNC structures [105]. In FTIR analysis, the peak shifts toward a higher wavenumber, accompanied by larger absorption peaks. This phenomenon shows that the mass of that molecule is reduced, which in this study shows the lower mass of the biMOF molecule compared to that of bi-MOF-rGO .[6] The presence of Zn and Co metals in the ZnCo bi-MOF-rGO structure can be further proven by the EDX results. In the EDX image presents the prominent peak corresponding to nitrogen provides additional evidence supporting the presence of N-doped GO. To study the interaction between the ZnCo MOF and rGO in the charge/discharge of the LASiS-synthesized HNC (Figure 4.5(c)), we

performed Ultraviolet-visible (UV-vis) spectroscopy. The wavelengths of the absorbent peak tend to shift toward the longer wavelength region and as the conjugated system becomes larger.[98] The shifts in UV-vis could be attributed to strengthening of the π bonds, as a decreased intermolecular force could cause an absorption UV peak to shift to a high wavenumber in the UV spectrum. These results show the existence of a stronger π - π interaction between bi-MOF and rGo. Coupling MOFs with GO through the π - π interaction is a commonly used method to increase the energy densities of electrochemical capacitors, but the low electron tunneling probability of the π - π interaction through the out-of-plane direction intrinsically limits the charge storage capacity and the charge/discharge rate.[?]] Therefore, porous carbon molecules are used in this study to increase the interaction of π - π through in-plane bond interactions, enabling exceptional charge storage performance by controlling the surface charge tunneling behavior of the molecule. In what follows, we discuss the results of our detailed structural characterizations of the previously mentioned MOF/bi-MOF-rGO samples, focusing on XRD analyses (see Figures 4.5 (a) and S4) for Zn and Co MOF-rGO and ZnCo bi-MOF-rGO using two different precursor salts, namely, $\text{Co}(\text{NO}_3)_2$ and CoCl_2 . To that end, the presence of sharp and distinctive peaks in the LASiS-synthesized MOFs-rGO and bi-MOF-rGO samples that closely match the simulated diffraction patterns of Zn and Co MOFs [73], confirms the existence of highly crystalline MOF phases. Figures 4.5(a) reveals the presence of XRD peaks attributed to the MOFs and biMOF-rGO crystals. However, presence of a slight shift to lower 2θ values in the XRD peaks suggest smaller pore sizes of ZnCo bi-MOF-rGO compared to Zn and Co MOF-rGO samples, validated by Brunauer-Emmett-Teller (BET) surface area analysis (See Figure 4.6). In addition, FTIR measurements identify the effective surface-specific functional groups present in these LASiS-synthesized MOF and bi-MOF-rGO HNCs. Figure 4.5(b) depicts the spectral features of the Zn MOF-rGO and the ZnCo bi-MOF-rGO compared to GO and the ZnCo bi-MOF. The spectral bands of 756 cm^{-1} are due to the 2-Methylimidazole (Hmim) out-of-plane bending ring, while the stretching at 1424 cm^{-1} is due to the in-plane bending [2]. Strong C-N vibrations at 1310 cm^{-1} , and C = N peaks at 1594 cm^{-1} [87]. Strong C-N vibrations at 1310 cm^{-1} and the C=N vibration at 1594 cm^{-1} indicate the presence of Hmim as a linker in the MOF structure. In general, the peak at $1250\text{-}1020\text{ cm}^{-1}$ is indicative of C-N stretching,

and at $1650\text{-}1580\text{ cm}^{-1}$ is a signature of N-H vibrations in the same structure or due to N-H bending in the Hmim molecule. Furthermore, the stretch of the aromatic ring in the imidazole structure is responsible for the weak peak at 1630 cm^{-1} . The strong metal linker bond, such as Co-N or Zn-N at 434 cm^{-1} confirms the presence of metal centers in MOF and MOF/biMOF-rGO HNC structures [105]. In FTIR analysis, the peak shifts toward a higher wavenumber, accompanied by larger absorption peaks. This phenomenon shows that the mass of that molecule is reduced, which in this study shows the lower mass of the biMOF molecule compared to that of bi-MOF-rGO.[6] The presence of Zn and Co metals in the ZnCo bi-MOF-rGO structure can be further proven by the EDX results. In the EDX image, the prominent peak corresponding to nitrogen provides additional evidence supporting the presence of N-doped GO. To study the interaction between the ZnCo MOF and rGO in the charge/discharge of the LASiS-synthesized HNC (Figure 4.5(c)), we performed Ultraviolet-visible (UV-vis) spectroscopy. A close inspection of the spectra reveals an absorbent peak shift toward the longer wavelength region. Also, commensurate with increase in size of the conjugated material, the absorption peaks become larger. [98] We attribute the shifts in UV-vis to strengthening of the π bonds, as a decrease in intermolecular force causes the absorption peak in the UV spectrum to shift to a higher wavenumber. Hence, These result clearly demonstrate the existence of a stronger π - π interaction between the bi-MOF and rGO. Coupling MOFs with rGO/GO through the π - π interaction is a commonly used method to increase the energy densities of electrochemical capacitors, but the low electron tunneling probability of the π - π interaction through the out-of-plane direction intrinsically limits the charge storage capacity and the charge/discharge rate.[?] Therefore, in this study, porous carbon molecules are used to increase the interaction of π - π through in-plane bond interactions, enabling exceptional charge storage performance by controlling the surface charge tunneling behavior of the molecule.

The BET study of the LASiS-derived samples shows a high surface area of the samples, which is around $1800\text{ m}^2/\text{g}$ (Figure 4.6(a), Table 1), while the highest pore volume and surface area belongs to the CoZn bi-MOF-rGO sample prepared using $\text{Co}(\text{NO}_3)_2$. The choice between using $\text{Co}(\text{NO}_3)_2$ and CoCl_2 precursors in LASiS-synthesized bi-MOFs introduces variations in pore sizes. Our previous work [87] provides a detailed explanation of the pore

size variation. Briefly, the change arises from factors such as the different anions (nitrate and chloride), each of which influences the coordination environment of cobalt ions in the MOF. The distinct solubilities, reactivities, and hydration between the nitrate and chloride further impact the kinetics of these bi-MOF formations, altering the nucleation and crystal growth rates. These nuances in precursor properties and their interactions with ligands lead to variations in MOF structures, supporting the importance of precursor selection in tailoring MOF and bi-MOF pore sizes for specific applications.

A larger surface area provides more sites for interaction between the MOF-rGO and the electrolyte, which is critical for energy storage devices. This increased interaction area allows for more electrochemical reactions, improving capacitance and energy storage performance. There is a correlation between capacitance and pore size at nanoscale, which is the capacitance increases with pore size. The pore size of MOFs composited with GO is a critical parameter that significantly influences their capacitance and energy storage performance in electrochemical systems. The pore size of MOFs directly affects the accessibility of active sites within the structure. MOFs with larger pores provide more space for ions and molecules to access these active sites. Therefore, larger pores allow for greater penetration and diffusion of ions into the MOF-based HNC, enhancing overall capacitance. Larger pores could give rise to more efficient use of active materials, resulting in higher energy storage capacity. In addition, larger pores facilitate faster ion movement, leading to rapid charging and discharging of MOF-based energy storage devices. This is especially critical in applications like SCs, where rapid energy storage and release are essential. On the contrary, smaller pores can hinder ion diffusion, limiting SC performance.

4.3.2 Electrochemical energy storage characterizations

In this section, we present the results of cyclic voltammetry (CV) measurements conducted at a scan rate of 20 mV/s, covering a potential range from -0.30 to 0.70 V. These measurements provide qualitative insights into the capacitive behaviors of the LASiS-synthesized MOF and bi-MOFs- rGO HNCs. Figure 4.7(a) shows the CV curves obtained in Na₂SO₄ electrolytes for different MOF and bi-MOF-rGO HNCs prepared using varying precursor salt. It is evident from the enclosed area under the CV curves that the effective

capacitance values exhibit a significant increase for bi-MOF-rGO samples synthesized using Co precursors compared to that of Zn MOF-rGO. This could happen because of the higher electrical conductivity and specific capacitance of ZnCo bi-MOFs compared to Zn MOF. The maximum capacitive value is observed for ZnCo bi-MOF-rGO prepared using $\text{Co}(\text{NO}_3)_2$ precursor and 10 minutes of ablation of a pure Zn pallet. This observation is further supported by galvanostatic charge/discharge (GCD) curves obtained at 1.0 A / g from GCD electrochemical measurements (Figure 4.7(b)), which demonstrate longer discharge durations (approximately 500 seconds) for HNC prepared with $\text{Co}(\text{NO}_3)_2$ salts. On the contrary, there is a drastic reduction in discharge times (less than 250 seconds) for HNCs synthesized without using any precursors and only by ablating the Zn pallet for 10 minutes.

The synthesis and role of the porous carbon (PC) material can be found in the supporting information section. An important insight from these results is the critical role of tuning the morphology and structure of these HNCs and finding the optimal amount of PC to maximize the functionality of these laser-produced MOF and bi-MOF nanostructures in the rGO/carbon matrix. These factors significantly affect the capacitive properties of the synthesized HNCs by altering the ion diffusion pathways, conductivity, and charge transport properties. A higher surface area of bi-MOF nanostructures provides a greater interfacial area for electrolyte interactions, facilitating the storage of more charges as a result of the increased faradaic reactions. However, beyond a critical concentration, charge transfer processes may be hindered due to the relatively low conductivity of the MOF species. The conductive nature of rGO is crucial for enhancing the non-faradaic supercapacitive properties of MOF-bi-MOF-rGO HNCs, enabling rapid charge transfer and improved electrode/electrolyte interfacial charge transport. The reason for selecting in-house synthesized functionalized PC as the C matrix of SC ink in this study is its higher surface area, better wettability, and higher conductivity compared to commercially available porous carbons (Figure 4.8).

The enhanced supercapacitance of ZnCo bi-MOF-rGO HNCs on a functionalized PC results from the integration of MOFs and rGO in the hybrid structure, which provides a high surface area and an extensive porous network, allowing for efficient ion adsorption and fast charge transfer, thereby increasing the capacitance. Furthermore, the synergistic effect between the MOF's pseudocapacitance and the rGO's double-layer capacitance results

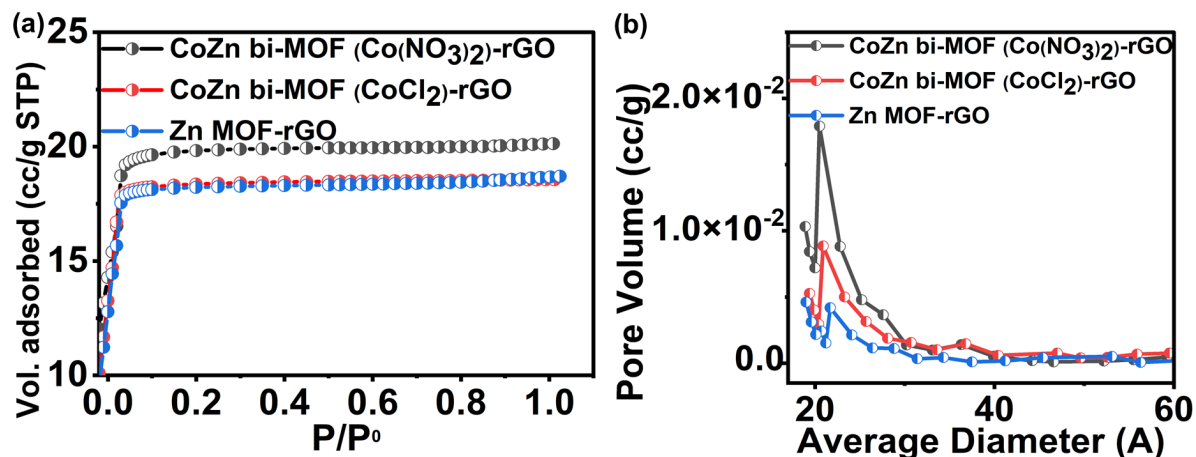


Figure 4.6: (a) Nitrogen gas adsorption isotherms at 77K and, (b) Incremental pore volume for Zn MOF-rGO, and ZnCo biMOF-rGO using Co(NO₃)₂ and CoCl₂ precursor salts.

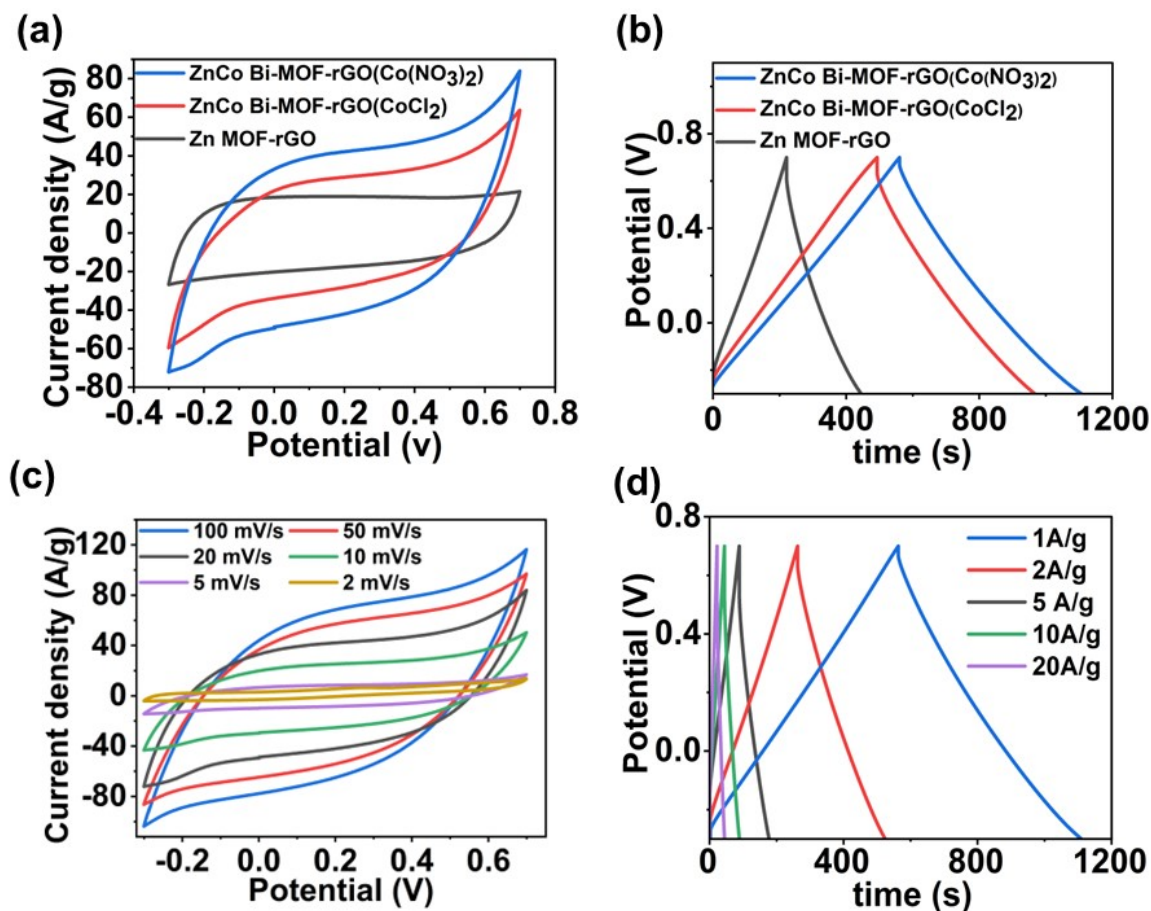


Figure 4.7: (a) CV and (b) CGD plot of Zn MOF-rGO, and ZnCo biMOF-rGO using Co(NO₃)₂ and CoCl₂ precursor salts. (c) Cv and (d) GCD ZnCo biMOF-rGO using Co(NO₃)₂ at different scan rate and specific current.

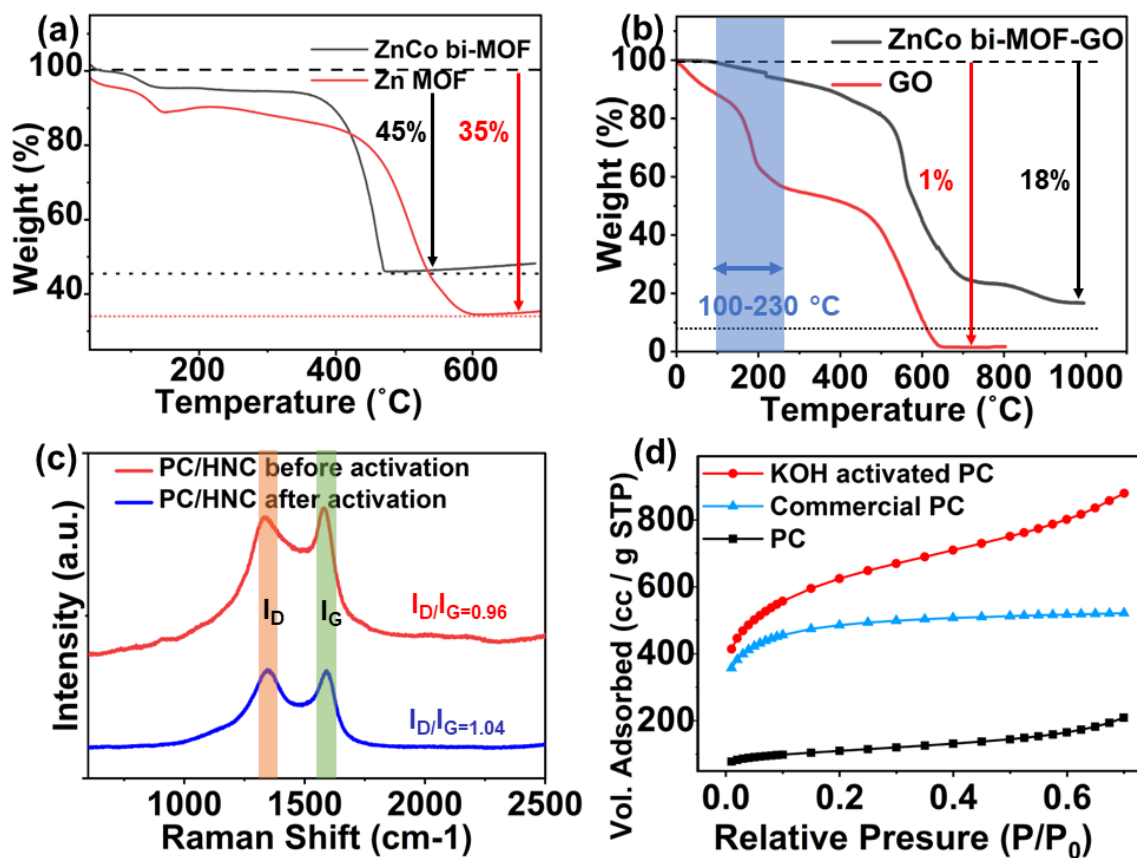


Figure 4.8: Thermal decomposition of (a) LASiS synthesized Zn MOF(red) and ZnCo bi-MOF(black) (b) GO (black), and ZnCo biMOF-rGO(red) *via* TGA, (c) Raman spectra of electrode material consisting LASiS synthesized bi-MOF-rGO HNC on functionalized and unfunctionalized porous carbon and (d) Adsorption isotherm of nitrogen (77K) on Functionalized, commercial and unfunctionalized porous carbons.

in combination of faradaic and non-faradaic charge storage that enhances the overall capacitance of the material.

The TGA plot in Figure 4.8 shows that HNCs have a different thermal behavior compared to MOFs and bi-MOFs, further supporting our claim that rGO covers the MOFs in the HNCs; hence, providing further proof for enhanced overall capacitance by leveraging both faradaic and non-faradaic charge storage mechanisms. The porous carbon substrate also provides structural support and enhanced electrical conductivity, facilitating rapid electron transport throughout the composite. The porous nature of the carbon matrix also promotes electrolyte penetration and ion diffusion, further enhancing the capacitive performance. Table 4.1 contains the porosity and BET surface area of MOF-bi-MOF-rGO HNCs, which shows that the highest value belongs to ZnCo biMOF-rGO using $\text{Co}(\text{NO}_3)_2$. Therefore, taken all together, the ZnCo bi-MOF-rGO HNCs on PC offer a high specific capacitance. To highlight the superior performance of this material, we have summarized the capacitance of typical MOFs and MOF-rGO as supercapacitor electrode material in Table 4.2.

4.3.3 3D-printed supercapacitor device

To investigate the thermal decomposition characteristics of MOFs, bi-MOFs, and MOF-bi-MOF-rGO HNCs during the annealing process of printed electrodes, we performed TGA experiments. Figure 4.8(a) depicts the TGA patterns for the Zn MOF and ZnCo bi-MOF obtained at a scan rate of $10^\circ\text{C}/\text{min}$ up to 700°C in N_2 medium. The initial weight loss, around $\sim 165^\circ\text{C}$ is due to solvent evaporation. The second weight loss in both MOF structures is associated with the partial carbonization of organic residuals within the MOF pores. As the temperature exceeds $400\text{-}500^\circ\text{C}$, the linker decomposes, leading to a partial collapse of the MOF structures, highlighting the high thermal stability of the LASiS synthesized MOFs and bi-MOFs. The remaining ~ 35 and 45 wt.% in each MOF structure corresponds to the formation of the respective metal oxides. TGA of HNCs also allows examination of the thermal stability of the 3D printed SC electrode material during the 80°C annealing treatments outlined in the printing process section above. Specifically, the TGA results presented in Figure 4.8(b) aim to characterize the thermal stability of the bi-MOF-rGO content in the ink material and the HNC structure. Initial mass loss around $100\text{-}200^\circ\text{C}$

results from the reduction of GO. A substantial mass change of approximately 60 wt% between 500 and 1000°C, signifies the degradation of the HNC. This validates that the HNCs employed in the printed SC ink, post-annealing, constitute approximately 20 wt% of the as-synthesized HNCs. Importantly, no significant mass change occurs in samples annealed at 100°C (Figure 4.8(b)), pointing to the fact that the bi-MOF-rGO HNCs do not undergo any thermal decomposition during the annealing process of the printing SC.

The Raman spectra of the bi-MOF-rGO HNCs on PC, before and after KOH functionalization, as depicted in Figure 4.8(c), reveal distinct peaks at 1356 and 1572 cm^{-1} corresponding to the D and G carbon peaks, respectively [106]. The ratio of I_D / I_G is indicative of the degree of graphitization, where a higher ratio indicates a higher degree of graphitization. Specifically, the A_{1g} vibration mode from phonon symmetry gives rise to the D peak, while the C_{sp^2} in-plane vibration of sp^2 carbon atoms from E_{2g} phonon mode vibrations produces the G peak. These results indicate the presence of carbon in both the graphitic and amorphous phases. The D/G peak intensity ratios (I_D/I_G) presented in Figure 4.8(c) offer a reliable estimate of the quantity of each phase in these materials. [108] A higher ratio (I_D/I_G) after KOH functionalization ($I_D/I_G=1.04$) compared to before functionalization of PC ($I_D/I_G=0.96$) signifies the existence of more disorder or defects resulting from the presence of amorphous carbon. This suggests that KOH, through the activation of PC, destroys more sites, leading to an increase in the porosity of carbon material. Specifically, breakage of micropores could lead to increased surface area of functionalized carbon. The data presented in Figure 4.8(d), and Table 4.1 clearly support this conjecture.

Electrochemical energy storage characterizations

In the ultimate step, we performed cyclic voltammetry (CV) measurements on the printed SC electrodes within a potential range of 0.0 to 0.80V at a scan rate of 50 mV/s (see Figure 4.9(a)). The advantages of preparing 3D printed SCs in this study include rapid prototyping of 3D electrode architectures and improved device performance. High porosity and large specific surface area are other significant benefits of 3D-printed electrodes, which not only can improve the contact area between electrodes and electrolytes but also can increase the

Table 4.1: The physical properties of BET Surface area, pore size, pore volume of MOF and Bi-MOFs on rGO. N₂ adsorption volume.

Sample	Surface Area (m ² /g)	Micropore Volume (cm ³ /g)	Micropore Area (m ² /g)
ZnCo bi-MOF-rGO (CoCl ₂)	1799.616	0.610819	1327.8374
ZnCo bi-MOF-rGO (Co(NO ₃) ₂)	1893.4045	0.662435	1438.6027
Zn MOF-rGO	1784.7748	0.609807	1325.8646
PC before functionalization	385.7247	0.059896	133.2701
PC after functionalization	2214.1902	0.318774	740.8546
Commercial PC	1685.4404	0.470045	1049.1171

Table 4.2: Comparison of various MOFs and MOFs-rGO as SC electrode material.

Electrode	Morphology (m ² /g)	Surface area	Capacity	Electrolyte	Ref.
Zn ZIF-8	Hexagonal	877	637.5 C/g at 10 A/g	0.35 M [K ₄ (Fe(CN) ₆)] .3H ₂ O in 6M NaOH	[114]
Zn ZIF-8	Rectangular plates	-	42.22F/g at 10 mV/s	6 M KOH	[113]
Co ₃ O ₄ -PANI@ ZIF-8 NPC NCs	rhombic dodecahedron	52.29	1407 F/g at 1A/g	3M KOH	[19]
Co MOF	Urchin-like	93.6	927 F/g at 0.25 A/g	3M KOH	[133]
Co ZIF-67	3D polyhedral shape	947	1014 F/g at 4.5 A/g	0.2 M K ₃ [Fe(CN) ₆] in 1 M Na ₂ SO ₄	[121]
Co ZIF-67-rGO	MOF crystals on sheet- rGO	571	1453 F/g at 4.5 A/g	0.2 M K ₃ [Fe(CN) ₆] in 1 M Na ₂ SO ₄	[121]
ZnCo biMOF -rGO HNC	membrane-like GO covered	1893.4	1092 F/g at 1 A/g	0.5 M Na ₂ SO ₄	this work

electrochemical performance. Furthermore, manufacturing the entire device *via* a 3D printing technique reduces the cost and complexity of manufacturing while increasing versatility and production capacity.

The resulting CV curves display characteristic profiles typically associated with materials exhibiting capacitive behavior, marked by a broadened current distribution. These observations signify pseudocapacitance performance, characterized by rapid reaction rates, attributed to the active ZnCo bi-MOF-rGO HNCs. Furthermore, CV analyses demonstrate an improvement in the capacitive properties of printed SCs incorporating the LASiS-synthesized ZnCo bi-MOF-rGO HNCs compared to those employing Zn MOF-rGO HNCs. The active layer composition of the SC electrode is 0.9 g graphene, 0.1 g porous carbon, and 0.2 g of either Zn MOF-rGO or ZnCo bi-MOF-rGO HNCs (see experimental section). The key distinguishing factor in the ink formulations is the presence of Co cations within the MOF structure of ZnCo bi-MOF-rGO HNC. Because HNCs comprise less than 20% of the total active layer composition, the capacitive performance of printed SCs containing Zn MOF-rGO and ZnCo bi-MOF-rGO does not show a substantial difference. However, it is noteworthy that the capacitive of enSC electrode material containing ZnCo bi-MOF-rGO is higher than Zn MOF-rGO HNC. We attribute the higher capacitance in the printed SC device containing ZnCo bi-MOF-rGO compared to that of Zn MOF-rGO to presence of Co. Evidently, Co enhances the electrochemical performance by introducing additional electroactive sites, thereby increasing the overall charge storage capacity. Co is known for its favorable redox properties, which could facilitate more efficient charge transfer processes and enhance the overall electrochemical performance of the active layer material. Also, the superior electronic conductivity of ZnCo bi-MOF is due to the presence Co and high electrical conductivity of elemental Zn, which contribute to an overall increase in both electrical conductivity and supercapacitive performance.^[123, 58]

Additionally, the galvanostatic charge-discharge (GCD) characteristics, with discharge currents set at 2.0 A / g, exhibit the expected SC behavior, as shown in Figure 4.9(b) for the printed SCs comprising LASiS-synthesized bi-MOF-rGO HNCs using $\text{Co}(\text{NO}_3)_2$ compared to SCs with single Zn MOF-rGO HNCs. The specific capacitance (C_{sp}), was calculated based on discharge characteristics. and its values for SCs incorporating single- and bi-MOF

MOF-rGO HNC materials synthesized with LASiS at a current density of 2.0 A/g during the discharge time were found to be 310 F/g and 670.5 F/g, respectively (see Figure 4.9(b)).

4.4 Summary

MOFs, known for their exceptional porosity, tunable pore size distribution, and structural adaptability, present a promising pathway for electrode materials in supercapacitors (SCs). Hence, MOFs combined with electrically conductive materials, such as rGO, result in high-performance hybrid nanocomposites (HNCs). To that end, MOFs composited with different allotropes of carbon result in high-performance electrode materials due to their hierarchical structure, high porosity, and excellent electrical conductivity. This study focuses on Zn MOF-rGO and ZnCo bi-MOF-rGO HNCs and presents a detailed analysis of their morphological, structural, and electrochemical properties. The results demonstrate remarkable specific capacitance and energy density by elucidating the significant role of π - π interactions in enhancing interfacial charge transfer processes and thus increasing the energy densities of these electrochemical SC devices. Furthermore, this study reveals that the presence of Co in the ZnCo bi-MOF-rGO HNC enhances electrochemical performance, namely, by increasing electroactive sites and improving conductivity, which result in higher capacitance compared to those of Zn MOF-rGO HNCs. In addition, we explicate the rationale for selection of in-house synthesized functionalized porous carbon as the carbon matrix for SC ink. Specifically, the in-house porous carbon leads to increased capacitance of SC, thereby improving its energy storage capabilities and overall performance. Specifically, the use of ZnCo bi-MOFs composited with rGO and in conjunction with carbon material allows the simultaneous realization of both pseudocapacitances through the metallic redox sites and double-layer capacitance, offering a versatile and efficient strategy for enhanced energy storage in SC applications.

Moreover, the study explores the domain of additive manufacturing and inkjet printing, investigating its potential applications in the fabrication of advanced SC devices. To that end, Zn MOF-rGO and ZnCo bi-MOF-rGO HNC electrodes are 3D printed using inkjet

printing techniques. The high specific capacitance and energy density of these HNCs set a benchmark for the excellent SC performance of inkjet-printed ZnCo bi-MOF-rGO HNCs. The findings of this study pave the way for the integration of MOF-rGO HNCs into advanced energy storage solutions, particularly in the world of 3D printed electronics, offering promising prospects for meeting the growing global demands for efficient and high-performance energy storage systems.

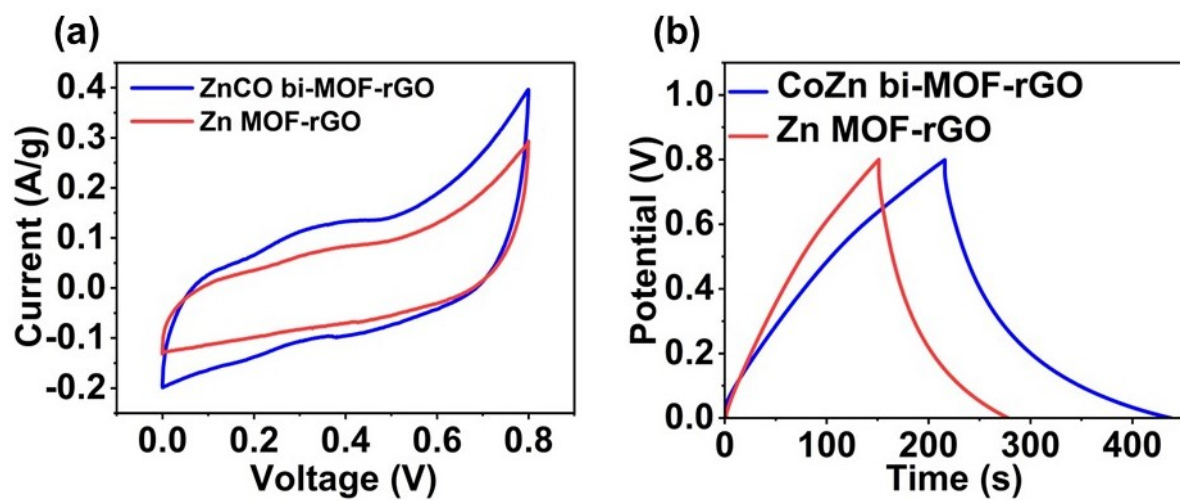


Figure 4.9: (a) CV (b) CD plots of Zn MOF-rGO, and ZnCo biMOF-rGO using $\text{Co}(\text{NO}_3)_2$ and CoCl_2 precursor salts.

Chapter 5

Conclusions and Future Directions

This dissertation explores the fabrication of functional hybrid nanocomposites using Laser Ablation Synthesis in Solution (LASiS). It specifically investigates the synthesis–structure–property relationships and their impact on electrochemical energy storage and conversion systems, focusing on Oxygen Reduction Reaction (ORR) electrocatalysis and Faradaic Supercapacitive devices. The research involves two main synthesis routes: Metal-Organic Frameworks (MOFs) and their composites, and reduced (rGO)/N-doped graphene-oxide and metal-oxide hybrid nanocomposites. Also, the thesis explores the fascinating world of supercapacitors (SCs) and their unique attributes, such as high-power density, long cycle life, and stability compared to lithium-ion batteries. Two distinct types of SCs, electrochemical double-layer capacitors (EDLC) and pseudo capacitors (PC), are discussed. The former utilizes activated carbon with a large surface area, while the latter employs graphene-based active layers, offering rapid and reversible charge storage. The study delves into the production of high-performance, economical, and eco-friendly supercapacitors. Various procedures for supercapacitor printing, including stacked designs and 3D electrode configurations, are also discussed in this thesis. The thesis emphasizes the need for innovative approaches in response to the rapid development of electronics, highlighting graphene-based electronics and 3D-printed graphene devices as promising solutions for achieving superior SC performance. Additionally, the integration of Metal-Organic Frameworks (MOFs) with carbon materials, specifically ZnCo bi-MOF-rGO hybrid nanocomposites, and their potential as high-performance electrode materials for SCs is demonstrated. The study concludes

by envisioning the future integration of MOF-rGO hybrid nanocomposites into advanced energy storage solutions, particularly within the field of 3D printed electronics, to meet the increasing global demands for efficient and high-performance energy storage systems.

This thesis also presents a groundbreaking method for the rapid synthesis of novel nano catalysts through a "green" synthesis approach, demonstrating the potential for efficient and cost-effective catalysts for oxygen reduction reactions in Alkaline Exchange Membrane Fuel Cells (AEMFCs). The study's findings offer valuable insights into the rational design of MOF-based functional nanostructures and underscore the significance of laser ablation synthesis in solution (LASiS) for synthesizing metal oxide-MOF@carbonaceous support matrices with diverse morphologies. The investigation of supercapacitive properties of hybrid nanocomposites of reduced graphene oxide (rGO) interfaced with nanostructured MnOx/Mn₃O₄, synthesized through Laser Ablation Synthesis in Solution (LASiS), adds another dimension to the research conducted. The study reveals that the ablation time during the LASiS process influences the structure-composition properties of the hybrid nanocomposites, which governs their characteristic capacitive behaviors. The electrochemical characterization of the all-printed supercapacitor electrode material fabricated from LASiS-derived MnOx/Mn₃O₄-rGO hybrid nanocomposites demonstrates superior specific capacitance, highlighting the potential of these materials for efficient energy storage.

Finally, the thesis discusses the broader landscape of printed supercapacitors, evaluating various materials and methods, including carbon-based materials, metal oxides, and metallic MOFs, combined with 3D printing, specifically inkjet printing, and direct ink writing techniques. The optimization of these techniques, along with ongoing advancements in electrode materials, is identified as pivotal to unlocking the full potential of printed supercapacitors in diverse energy storage applications.

5.1 Proposed Future Work

The proposed future work involves expanding the fabrication of HNCs beyond laboratory-scale and integrating them into next-generation devices for space exploration, exploring 3D

printing technology for on-demand devices in space missions, with a focus on LASiS-produced ternary metal oxides/rGO HNCs for solid-state faradaic supercapacitors.

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Vita

Mahshid, originally from Urmia, West Azerbaijan, Iran, embarked on her Ph.D. journey in Chemical and Biomolecular Engineering at the University of Tennessee, Knoxville, in 2020. Her academic background is rooted in atomic and molecular physics, and she has a Master's degree from the University of Tabriz, Iran, specializing in Laser Physics. Throughout her academic journey, Mahshid's research has focused on synthesizing functional nanomaterials, employing laser ablation synthesis in solution. Her Ph.D. work has particularly centered on exploring the energy applications of these nanomaterials. During her time at UTK, Mahshid garnered several prestigious awards, including the Carbon Nanomaterials: Graduate Student Award in Nanoscale Science and Engineering Forum during the American Institute of Chemical Engineers (AIChE) 2022 conference in Phoenix, Arizona. Her work also achieved first place in the Materials Engineering and Sciences poster session at the AIChE 2023 conference in Orlando, Florida, and received the Graduate Research Mentor Award at the Faculty Research Mentor Award recognition session in the Spring of 2023 Exhibition of Undergraduate Research and Creative Achievement (EUR̄CA) event, highlighting her commitment to guide and support fellow researchers. She also received the Exceptional Progress Award for Outstanding Third-Year Graduate student, recognizing her accomplishments and the research's originality, dedication, and potential merit. These accolades underscore Mahshid's commitment to excellence and collaboration within the academic community.