

Redox-active 2D Covalent Organic Frameworks for Energy Storage and Proton Conduction

विद्या वाचस्पति की

उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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PUNE 2023

Dedicated to
My parent and family members



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Certified that the work incorporated in the thesis entitled “**Redox-active 2D Covalent Organic Frameworks for Energy Storage and Proton Conduction**” submitted by **Mr. Rinku** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.

Date: 08th September 2023

Place: Pune

Prof. R. Vaidhyanathan
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Mr. Rinku

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List of Acronyms

Materials related	Units
COF: Covalent Organic Frameworks	°C: Degree Celsius
CON: Covalent Organic Nanosheets	mmol: Milli moles
MOF: Metal Organic Framework	hrs: hours
CP: Coordination Polymer	μL: Microliter
HCPs: Hyper-crosslinked polymers	μm: micrometer
POPs: porous organic polymers	mL: Milliliter
Instrument and measurement related	nm: nanometer
FE-SEM: Field Emission-Scanning Electron,	min: Minutes
HR-TEM: High Resolution Transmission Electron Microscopy	mol: moles
SAED: Selected Area Electron Diffraction	gm: Gram
TGA: Thermogravimetric analysis	Å: Angstrom
PXRD: Powder X-Ray Diffraction	MHz: Megahertz
SCXRD: Single Crystal X-ray diffraction	V: volts
AFM: Atomic Force Microscopy	mV: Millivolts
BET: Brunauer Emmett Teller	M: Molar
GCD: Galvanostatic charge-discharge	A: Ampere
EDLC: Electrical Double Layer Capacitance	mA: Milliampere
CE: Counter Electrode	F: Faraday
Csp: specific capacitance	mg: Milligram
WE: Working Electrode	K: Kelvin
RE: Reference Electrode	mA/g: milliamperes/gram
CV: Cyclic Voltammogram	mAh/g: milliamperes hour/gram
Chemicals related	CC: Cubic Centimeter
DMF: N, N-Dimethyl formamide	RH: Relative Humidity
DMSO: Dimethyl sulfoxide	RT: Room Temperature
NMP: N-Methyl-2-pyrrolidone	S/cm: Siemen per Centimeter
ACN: Acetonitrile	σ: Ionic conductivity

List of Acronyms

EtOH: Ethanol	Z: Impedance
H ₂ SO ₄ : Sulphuric Acid	R: Resistance
THF: Tetrahydrofuran	ppm: parts per million
tBu-NH ₄ PF ₆ : Tetrabutylammonium phosphate	mW/cm ² : mili-Watt per centimeter square
MeOH: Methanol	Ea: Activation Energy
HCl: Hydrochloric acid	DFT-TB: Tight Binding Density Functional Theory
H ⁺ : Hydrogen ion, Zn ⁺² : Zinc ion, K ⁺ : Potassium ion	eV: electron volt
H ₃ PO ₄ : Phosphoric acid	CPE: Constant Phase Element

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Redox-active 2D Covalent Organic Frameworks for Energy Storage and Proton Conduction

Synopsis

Chapter 1: Introduction

Covalent Organic Frameworks (COFs) are a new class of crystalline polymers constructed using reticular chemistry. The functionalizable precursors connected by covalent bonds give rise to graphene-like 2D layers. These layers π stack to generate a stacked-layered structure resembling graphite but with accessible pores. Their distinctive properties include crystalline structure, high surface area, structural versatility, easy surface modification, tunable pore size, and excellent thermal and chemical stability. These properties make COF an interesting candidate for various applications such as energy storage, optoelectronic devices, gas separation, heterogeneous catalysis, sensing, etc. COFs can serve as a good alternative to heteroatom-doped graphite materials for charge storage and conduction. The precise installation of heteroatoms in the COF backbone can boost the performance. In the design, redox-active groups are incorporated into the COFs to make them more suitable for supercapacitors, metal-ion batteries, and ion conduction. The presence of redox-active functional groups (carbonyl, hydroxyl, pyridine, triazole, tetrazine, etc.) stores additional charges via Faradaic processes and also helps in its fast percolation. Additionally, the redox-active supporting electrolytes adsorbed or anchored on the COF would provide a significant advantage in the performance. In most cases, the COF functions not as a mere support but as a synergistic active participant.

The energy devices such as capacitors, batteries, or fuel cells usually power electronic devices at the circuit level. In the first two cases (capacitors, batteries), the stored energy generates an electric potential that drives a directional flow of electrons during charging or discharging, generating an electric current. However, in the case of fuel cells, it is an electrochemical energy

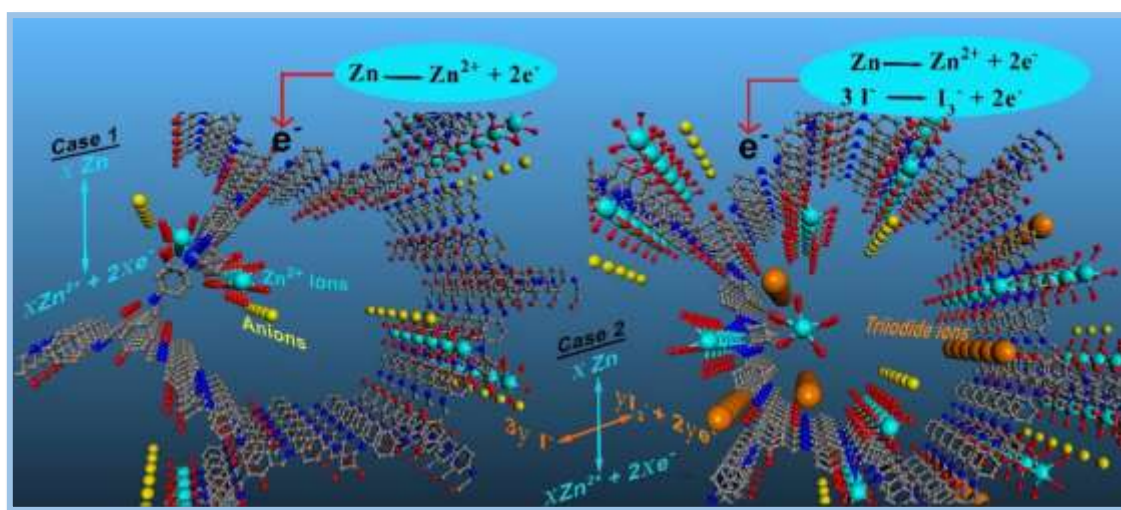
conversion device that directly converts the chemical energy of a fuel and oxidant into electrical energy. These energy storage and conversion devices are fundamental to powering various electronic devices and ensuring their efficiency in modern lifestyles. These energy storage devices are classified based on two fundamental parameters: energy density and power density. Capacitors have lower energy density as they store energy in an electrostatic field while offering exceptionally high power density, making them suitable for delivering rapid bursts of power for short periods. Batteries provide higher energy density than capacitors as they store energy electrochemically but have moderate power density. They are well-suited for applications that require sustained power output. Fuel cells, on the other hand, boast the highest energy density among the three, generating electrical energy through electrochemical reactions. While they have moderate power density, they deliver sustained and high-energy output over prolonged periods. The selection of the appropriate energy storage device depends on the explicit needs and demands of the application, with capacitors, batteries, and fuel cells offering distinct advantages for various use cases. Being built from low atomic weight elements such as C, H, N, O, S, etc., COFs inherently offer a gravimetric advantage leading to superior energy and power density. In this thesis, we have redox-active functional groups (carbonyl, hydroxyl, pyridine, triazole, triazine, etc.) decorate the pores' walls of porous COFs to make them suitable for supercapacitors, batteries, and fuel cell membranes. In the first two chapters, redox electrolyte was utilized with porous COF to enhance the performance of supercapacitor and Zn-ion battery.

Chapter 2: Exceptional Capacitance Enhancement of a Non-Conducting COF through Potential-Driven Chemical Modulation by Redox Electrolyte.



In this chapter, we synthesized IISERP-COF25 and utilized this for supercapacitor application. KI as a redox-active electrolyte was combined in an H_2SO_4 electrolyte for the first time with the COF-based electrode. This composite electrode benefits from the redox-functionality of COF and the electronic conductivity of carbon, leading to superior capacitive activity. Operando spectro-electrochemical measurements (Insitu Raman and Insitu UV-Vis) reveal the existence of multiple polyiodide species, although the I_3^- is the predominantly electroactive species adsorbing on the microporous triazine-phenol COF electrode. A systematic fabrication of the flexible solid-state devices using the COF-redox-electrolyte reveals a high areal capacitance of $270 \pm 11 \text{ mF cm}^{-2}$ and gravimetric capacitance of $57 \pm 8 \text{ F g}^{-1}$. The inclusion of KI in H_2SO_4 (electrolyte) yields an approximately eight-fold enhancement in solid-state gravimetric specific capacitance. Remarkably, the imine-COF retains 89% of its capacity even after 10,000 cycles.

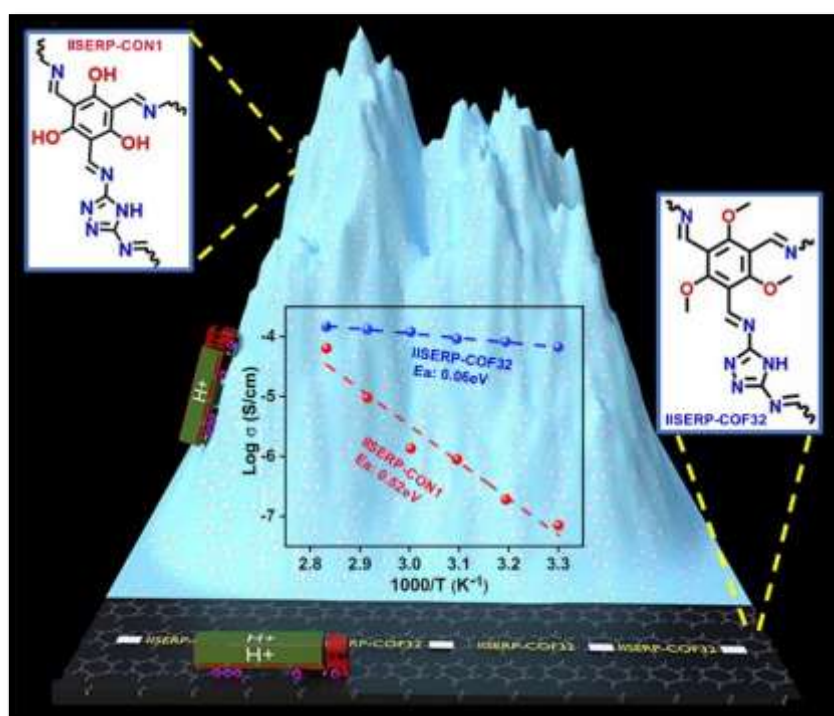
Chapter 3: Made to Measure Squaramide COF Cathode for Zn Dual-Ion Battery with Enriched Storage via Redox Electrolyte



In this chapter, we have discussed about a COF-derived Zn-ion battery. Aqueous rechargeable batteries are promising grid-scale energy storage devices because of their affordability, operational safety, and environmental benignity. Among these, Zn-ion batteries (ZIBs) have unfolded new horizons and are argued to be a potential replacement for Li-ion batteries, at least in stationary energy storage. For practical reasons, designing superior cathodes for ZIBs is crucial. Covalent organic frameworks (COFs) can be made redox active with a high storage surface. Here, for the first time, a chelating COF with redox-active ZnI_2 in a $\text{ZnSO}_4(\text{aq})$ electrolyte is combined. Including iodide harvests an approximately threefold enhancement in

capacity from 208 to 690 mAh g⁻¹ at 1.5 A g⁻¹, till date, the highest among all the COF-derived ZIBs. Remarkably, a charge–discharge curve at 1.3 V exhibits very limited dropout voltage and super-flat platform, with a noteworthy capacity of 600 mAh g⁻¹ at 5 A g⁻¹ stable up to 6000 cycles, confirming that the polyiodide generation and storage are sustainable. Additionally, rendered as a flexible Zn-ion battery, it displays a capacity of 590 mAh/g. The COF's dual-ion storage (Zn²⁺ and polyiodide) delivers a ZIB with the highest energy density. Spectro-electrochemical measurements coupled with X-ray photoelectron spectroscopy unambiguously unveil the existence of multiple polyiodide species, with I₃⁻ and IO₃⁻ ions as the prominent species. The latter gets reduced at the COF electrode under an applied potential, leaving I₃⁻ as the major species stored on the COF. The inclusion of polyiodides injects additional ion-electrons into the system resulting in higher energy density.

Chapter 4: Transformation of Covalent Organic Nanosheets to Covalent Organic Framework via Molecular Design to Achieve High Room Temperature Proton Conduction



In this chapter, we propose to investigate the relationships between Covalent Organic Nanosheets (CON) vs. COF for proton conduction application via molecular-level tuning with hydroxyl vs. methoxy functional groups, IISERP-CON1 and IISERP-COF32 respectively. CONs are exfoliated forms of COF and tend to be less crystalline. In our study, modifying the

–OH groups in the framework of a CON with a methoxy group, transforms the CON into COF and imparts long-range ordering visibly seen as improved crystallinity. To demonstrate the advantage this boosted crystallinity can provide to ion-conduction, we investigated the proton conductivity of $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ and $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ from room temperature 25 to 80 °C under 90% RH (relative humidity). They showed a proton conductivity of $7.85 \times 10^{-4} \text{ S cm}^{-1}$ and $1.53 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature for H_3PO_4 -loaded CON and COF, respectively. Finally, to validate its performance in a fuel cell set-up, a membrane electrode assembly (MEA) comprised of COF membrane was subjected to single-cell testing under real proton exchange membrane (PEM) operating conditions. The current density and maximum power density achieved by the COF membrane were approximately 965 mA cm^{-2} and 218 mW cm^{-2} , respectively, with the lowest Pt/C loading of 0.25 mg cm^{-2} by decal method. Recently, Zhang and co-workers reported a COF-based membrane that achieved a maximum power of 135 mW cm^{-2} and a maximum current density of 676 mA cm^{-2} with Pt/C loading of 1 mg cm^{-2} , which has been the best COF-based membrane. Therefore, we have the highest performance among all the COF-based membranes, with the lowest Pt/C loading reported for fuel cell applications.

INTRODUCTION

Synthetic organic polymers are extensively utilized in various aspects of modern life due to their diverse and advantageous properties. However, achieving a systematic illumination of the structure-property correlation of these polymers requires better control over the process of polymerization, topology, morphology, and directional growth. This can be achieved through a pragmatic, experimental approach, which involves a more appropriate choice of cross-linking and π -stacking monomers, leading to a highly ordered crystalline structure favorable for computational studies, which could lead to futuristic technological advantages.¹

The precise integration of monomeric units is necessary to achieve a high degree of polymerization with controlled directionality and impart structural periodicity. However, achieving controlled growth of the polymeric skeleton while maintaining proper geometry, porosity, and molecular-level properties is challenging.²

1.1 Linear Polymers:

Linear polymers are an important class of macromolecules that exhibit a linear, unbranched chain-like structure. They are widely used in diverse industries due to their remarkable properties and versatility. Linear polymers consist of repeating units called monomers linked by covalent bonds to form a long, unbranched chain. The monomers can be identical or different, depending on the specific polymer.³ The linear chain structure allows for the alignment of polymer chains, directing to self-organized and elongated networks. Linear polymers possess a straightforward yet versatile structure, offering a wide range of properties that make them useful in numerous applications across different industries. Understanding the structure-property relationships of linear polymers facilitates scientists and engineers to design and tailor polymers with specific features, leading to further advancements in materials science and technology. Linear polymers have found significant applications in various fields, playing critical roles in packaging materials, textiles and fibres, adhesives and coatings, biomedical applications, and electrical insulation.⁴ These applications highlight the versatility and importance of these polymers in various industries. However, the absence of adequate porous volume limits the application of these materials in areas such as gas storage, separation, charge storage, and various other separation processes. Consequently, there is a need to substitute hyper-crosslinked or porous polymers to overcome this limitation.⁵

1.1.1. Hyper-Crosslinked Polymers or Porous Organic Polymers:

Hyper-crosslinked polymers (HCPs) and porous organic polymers (POPs) are another porous material class that has gained significant attention among material chemists. These materials exhibit unique properties, such as high surface area, tunable porosity, and excellent chemical stability, making them suitable for a wide range of advanced applications beyond linear polymers. Hyper-crosslinked polymers and porous organic polymers (POPs) could be two-dimensional or three-dimensional networks formed by the reaction of aromatic or aliphatic monomers that incorporate organic building blocks.⁶ The crosslinking creates a rigid and highly interconnected structure, substantially increasing surface area and porosity compared to linear polymers. These polymers could have conjugation or maybe non-conjugated, depending on the choice of monomers and the type of linkage chemistry HCPs and POPs can be synthesized through various methods, including Friedel-Crafts alkylation, Friedel-Crafts acylation, condensation polymerization, or copolymerization of suitable monomers.⁷ These reactions often involve aromatic or aliphatic compounds with functional groups facilitating crosslinking. Hyper-crosslinked POPs have emerged as promising porous materials with exceptional chemical stability finding application various gas storage and separation applications, catalysis, energy storage, adsorbents for environmental remediation, and sensing and detection. These applications highlight the versatility and potential of HCPs and POPs in addressing key challenges and advancing various fields of research and technology compared with linear polymers.⁸

However, the absence of crystallinity in these materials poses challenges when it comes to understanding their structure and properties relationship. Additionally, they do not provide adept control over pore size, surface area, and other desired characteristics. The classical linear polymers are grown as liquid crystal polymers, which are typically grown on a substrate. Growing bulk cross-linked polymers with such a degree of crystallinity-driven order is highly desirable. This led to covalent organic frameworks (COFs) – crystalline bulk polymers. COFs offer enhanced structural control, well-defined porosity, and tunable properties, making them a promising alternative in miscellaneous applications.⁹

1.2. Covalent Organic Frameworks (COFs):

Covalent Organic Frameworks (COFs) are a new class of porous materials consisting of ordered arrays of organic molecules covalently linked together in a crystalline structure. These materials form a network of solids, wherein the constituent building blocks establish covalent bonds, constituting a two or three-dimensional network and held together by weaker intermolecular forces such as hydrogen bonding or van der Waals forces and π - π stacking to provide extra stability. COFs were initially proposed in 2005 by Prof. Omar Yaghi and his research group.¹⁰ Since then, these frameworks have captivated the attention of materials scientists due to their exceptional attributes: notable surface area, significant porosity, and modifiable chemical and physical traits. COFs have potential applications in numerous fields, such as gas storage and separation, catalysis, energy storage, charge conduction, and electronics.^{11,12} The composition of COFs generally comprises small organic molecules incorporating functional groups such as boronic acid, phenyl acetonitrile, imine, or amide groups and linked through using Schiff base condensation, boronate ester formation, carbon-carbon (sp^2) bonding, or imine formation (Figure 1.1). Choosing suitable monomers and reaction conditions allows control over pore dimensions, surface area, and other desired functionalities for specific applications, thereby dictating the resulting topology (Figure 1.2). The design of COFs at the molecular level diverges significantly, enabling precise manipulation of both primary and higher-order arrangements to an unparalleled degree. The proper templated synthesis of COFs generates confined void space and exposed surface to interplay with photons-excitons, electrons holes, ions, and molecules, creating a new molecular platform for developing materials for applications that interconnect materials chemistry, physics, and technology.^{13,14}

The stability of COFs is crucial for their practical applications and performance. They are known for their strong covalent bonding, which gives them an edge over other porous materials like MOFs or zeolites. Despite their impressive stability, some challenges include structural collapse via acid/base hydrolysis, susceptibility to specific reactants (strong oxidizing and reducing agents), and limited tolerance to extreme conditions (heat and pressure). However, majority of such observations are from the early boronic acid and ubiquitous imine-bonded COFs. Therefore, comprehending the robustness of COFs is vital for effectively using them across various applications. Given the expanse of covalent bonding chemistry, still there is a lot of room to play with.¹⁵

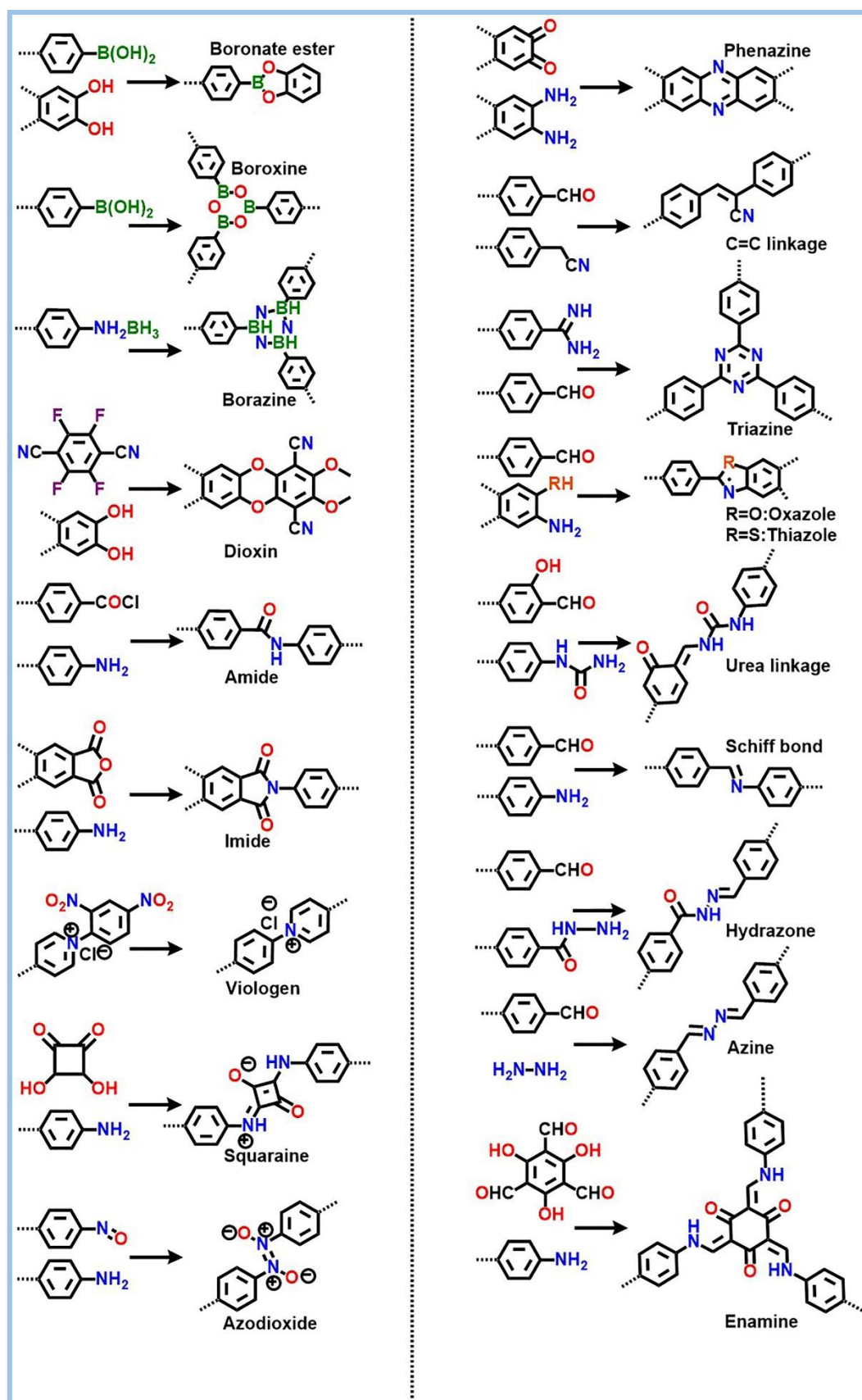


Figure 1.1. Monomeric building unit for COF formation. The shaded area shows Schiff base chemistry to develop frameworks.

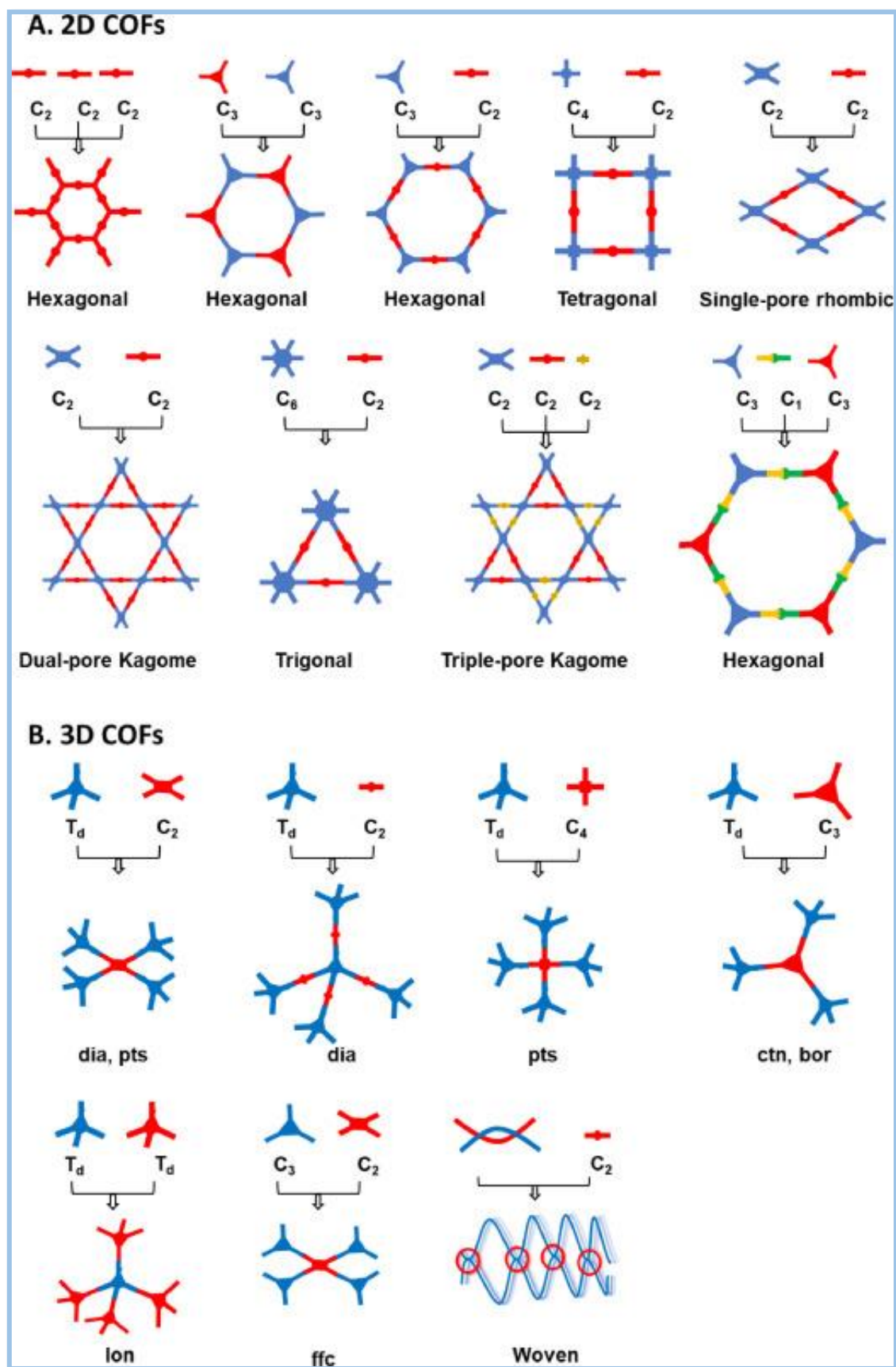


Figure 1.2. Topology diagrams representing a general basis for COF design and construction of (A) 2D COFs and (B) 3D COFs (Adapted from ref. 16).

1.3.1. Advantages of Covalent Organic Frameworks (COFs):

Covalent Organic Frameworks (COFs) exhibit distinct advantages that position them as a promising class of materials with diverse applications across various technological fields.^{17,18} Here we list some of the well-established features of COF.

1.3.1.1. Design Flexibility: COFs offer unparalleled design flexibility compared to other porous materials like zeolites and metal-organic frameworks (MOFs). Their modular and reticular structures allow for precise control over their composition, shape, pore size, and surface functionality, making it possible to tailor COFs for specific applications. Typically, being built from aromatic rings, there are multiple sites to incorporate functional groups on-demand. Also, employing large aromatic units, electron-withdrawing and electron-donating units enables a good route to introducing redox-, photo- and catalytic- activity and metal-specific binding sites.

1.3.1.2. Chemical Stability: COFs are formed by strong covalent bonds, imparting superior chemical stability. Unlike MOFs that might be susceptible to framework collapse or degradation under certain chemical conditions, COFs built from appropriate covalent bonds can withstand extreme environments without compromising their structural integrity.

1.3.1.3. High Surface Area: COFs possess a high surface area due to longer building units and their well-defined and ordered pore structures. This attribute enhances their capacity for gas adsorption, rendering them highly efficient for gas and charge storage applications. Also, when decorated with pre-coded binding centers or reactive centers, the high surface area and orderliness ensures their facile access and participation. In many cases, this makes COF an excellent support as well, in which case the active centers are directly integrated into the COF through bonds, or composited.

1.3.1.4. Customizable Pore Size: The tunable pore size COFs allow selective adsorption of specific ions, molecules or gases. This capability proves advantageous for separation processes, such as gas purification, environmental remediation, charge storage, and conduction applications. By right choice of monomer's size, geometry, and self-organization capability the pore size can be tailor made for the guests of choice.

1.3.1.5. Tunable functionality offered by COF: COFs are highly versatile materials that offer tunable functionality, providing a unique advantage in tailoring their properties for specific applications. This provides the ability to incorporate various functional groups into

their framework during synthesis or through post-synthetic modifications to fulfil specific requirements (Figure 1.1.). Some key aspects of tunable functionality in COFs include. Introducing conjugated functional groups or nanoparticles into COFs can modify their electrical and optical properties. This tunability opens up opportunities for applications in electronics, optoelectronics, and photonics. Incorporating redox-active groups into COFs facilitates electron transfer reactions, leading to potential applications in energy storage, electrocatalysis, and batteries.^{19,20}

1.3.1.6. High thermal and chemical stability of COF: COFs demonstrate excellent thermal stability and remarkable chemical stability due to the nature of their covalent linkages. The strong chemical bonds between the organic building blocks allow COFs to withstand elevated temperatures and exposure to a wide range of harsh chemical environments without undergoing structural degradation. This thermal robustness and chemical stability make COFs suitable for applications that involve high-temperature processes, such as catalysis, gas storage, and separation.

1.3.1.7. Environment-friendly and non-toxic nature of COF: COFs are environmentally friendly and non-toxic materials. They predominantly comprise organic building units, making them durable and biocompatible. COFs do not contain toxic metals or harmful substances, ensuring their safe use in various applications, including drug delivery, water purification, and electronics. This makes COFs promising candidates for addressing environmental challenges and advancing green technologies.²¹

1.3.2. Strategies for Designing Schiff bond-based COFs:

Condensation reactions are the primary method to create COFs with diverse heteroatoms and multiple functional groups. The presence of labile bonds can lead to the breakdown of the COF structure, resulting in a loss of porosity and degeneration of its properties. Boronic acid-based COFs are known to exhibit poor hydrolytic stability.²² The hydrolysis of boronic acid linkages in COFs occurs through the cleavage of the B-O bond, yielding boronic acid diol and regenerating the parent building blocks. This process disrupts the structural arrangement, leading to the collapse of its ordered structure and the possible leaching of the boronic acid units into the surrounding environment. To mitigate the limitations associated with boronic acid-based COFs, Schiff bond-based COFs have garnered substantial attention. Schiff bond linkages offer a promising alternative to address the challenges posed by boronic acid-based

COFs. Their benefits are manifold and have contributed to their popularity in COF research. One significant advantage is their enhanced hydrolytic stability compared to boronic acid linkages. This stability is crucial for applications in aqueous or humid conditions, where maintaining COF structural integrity is paramount. This enhanced stability is critical for applications in aqueous or humid environments, where the COF's structural integrity is essential. The widespread application of Schiff-base condensation reactions or dynamic imine-bond connectivity stands out of all these methods. It has grasped the interest of materials researchers due to specific characteristics.²⁴

1.3.2.1. Ease of Synthesis:

Schiff-based COFs can be synthesized through simple and well-established condensation reactions between the library of aldehydes and amines. This ease of synthesis allows for efficient and scalable production of COFs.²⁵

1.3.2.2. Versatility in Building Blocks:

The vast library of aldehydes and amines available for Schiff-base chemistry provides a broad range of building block combinations, offering flexibility in designing noble COFs with specific structures and properties.

1.3.2.3. Stability of Schiff bond:

Schiff-based COFs exhibit good chemical stability, allowing them to withstand various environmental conditions, including Hydrolytic and thermal stability, and maintain their structural integrity in practical applications compared with others.

1.3.2.4. Dynamic Chemistry:

Schiff-based COFs can display dynamic properties due to reversible covalent bonding, enabling responsiveness to external stimuli and potential applications in self-healing materials. Dynamic bond repairing helps for improving the crystallinity of COF. It can lead to the formation of a proper single crystal of COF. Yaghi and co-workers achieved a significant breakthrough in the field of COFs by successfully obtaining single crystals of a Schiff-based COF material using dynamic chemistry.²⁶ In their research, they employed aniline as a

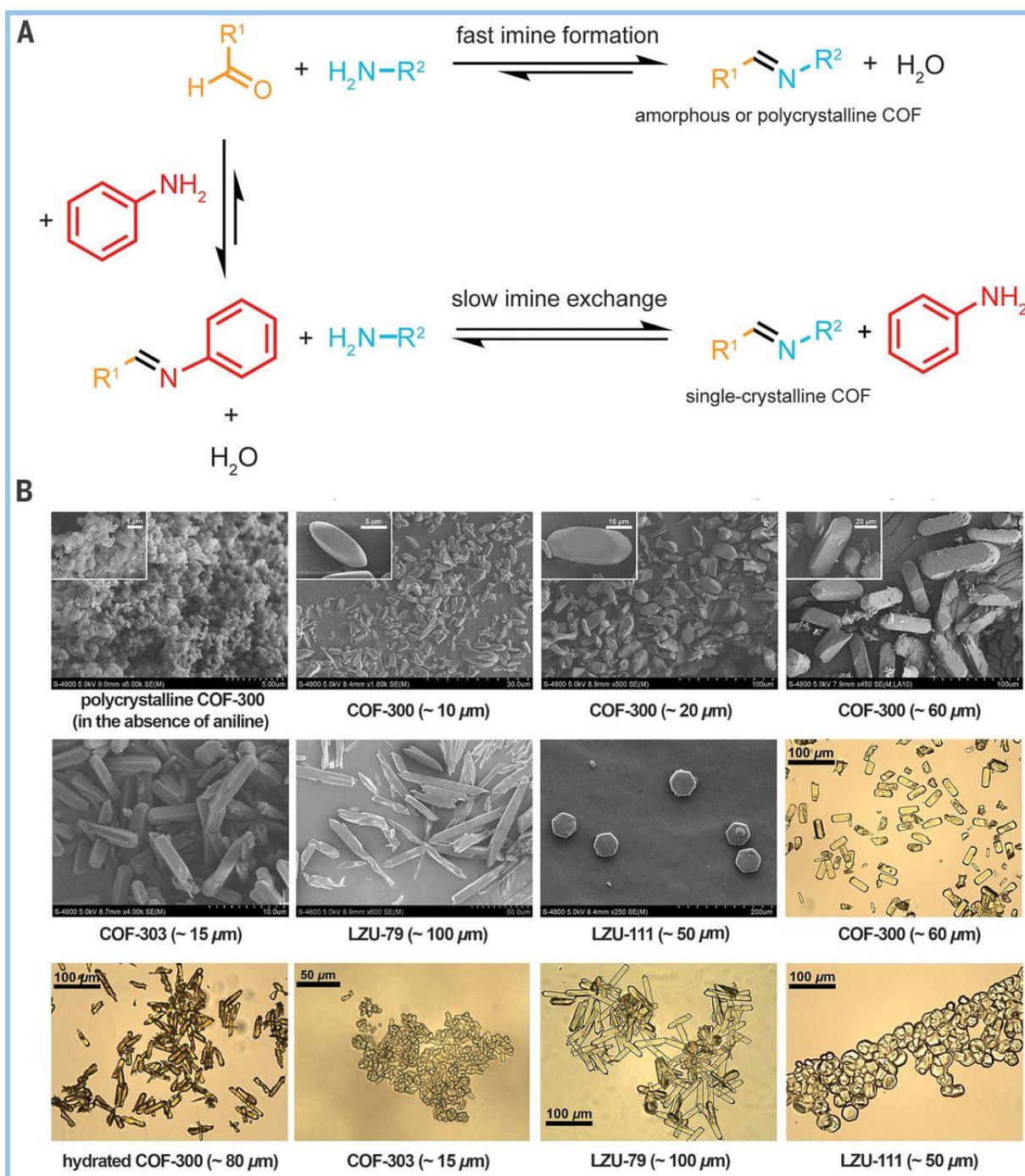


Figure 1.3. Single Crystal development of COFs regulated by aniline. (A) In the absence of aniline, the equilibrium shifts toward the product, polycrystalline or amorphous COFs, during the formation of imine bonds. The initial imine bond formation is fairly quick in the presence of aniline; however, slow imine exchange promotes the production of single-crystalline COFs. (B) Images of single-crystalline COFs obtained using optical and SEM microscopy in the presence of aniline, and whose structures were clarified and solved in this research. For comparison, the polycrystalline COF-300 SEM picture without aniline is shown. (Adapted from ref. 26).

modulator, which initially reacted with the aldehyde and then reacted with the amine-building unit in a slow and controlled manner. This unique approach facilitated the growth of single-

crystalline COFs. Using aniline as a modulator played a pivotal role in promoting the formation of single crystals, allowing for the first detailed structural analysis of a COF using single-crystal X-ray diffraction. This advanced technique provided precise information about the atomic arrangement and connectivity within the COF structure, enabling successful solving and refining the obtained single-crystal COF. Yaghi and his team's research represent a significant milestone in COF studies, as it showcases the importance of dynamic bond formation in achieving single-crystal structures and unveils new opportunities for exact structural insights.

1.3.3. Imparting Stability by Strengthening the Covalent Linkage:

While Schiff bond-based Covalent Organic Frameworks (COFs) are chemically robust and more stable than boronic acid-based COFs, they can be susceptible to hydrolysis when exposed to acidic or basic environments or even ambient moisture. Therefore, the formation of thermodynamically stable crystalline structures does not guarantee their robustness. Strengthening the COF framework with resistive functionality becomes essential to improve chemical stability. For further improvement of the strength of Schiff bond-based COFs, enhancing their performance and expanding their practical applications is crucial, especially for charge storage and conduction applications. Here are strategies that can be employed to achieve excellent stability.²⁷

A strategically design building can transform a reversible Schiff base bond to an irreversible Schiff base bond through keto tautomerization of the β -ketamine unit present in the backbone of the structure. The irreversible transformation of enolic bonds to the corresponding keto form significantly enhances the chemical stability of the COFs. This conversion involves changing the Schiff base double bond ($-C=N-$) to a single bond ($=C-NH-$) and forming a highly stable six-member interlayer hydrogen bond (Figure 1.4.).²⁸ This hydrogen bond provides electronic shielding, protecting the COF structure from collapse. Remarkably, this irreversible tautomerization does not alter the COF's crystallinity. The transformation involves only shifting the electron cloud from the enol group to the adjacent Schiff-base bond in the beta position while keeping the atomic locations nearly unchanged.

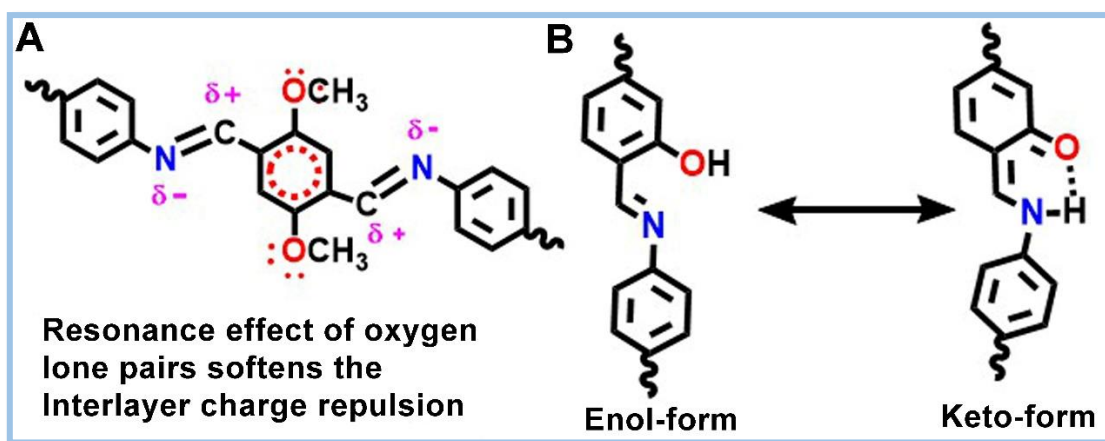


Figure 1.4. (A) Stability introduced due to the resonance effect of due to lone pairs the oxygen, weakens the polarization of the $\text{C}=\text{N}$ bonds and softens the COF's interlayer repulsion. (B) Six-membered ring formation due to the H-bonding ability of the keto form of the β -ketamine.

Consequently, COFs built from the β -ketamine linkage are highly suitable for electrochemical applications. Even when subjected to broad potential sweeps and in the presence of redox-active electrolytes, these COFs demonstrate excellent robustness compared to other COFs. The combination of reversible Schiff base formation and irreversible keto tautomerization offers a promising approach to enhance the stability and utility of Schiff bond-based COFs in various electrochemical applications. Jiang and colleagues created the highly chemically stable COF, TPB-DMTP-COF (Figure 1.4), by condensation of 1,3,5-tri-(4-aminophenyl) benzene (TAPB) and dimethoxy terephthalaldehyde (DMTP), to alleviate the repulsion of the COF interlayer. Electrostatic interlayer repulsion is reduced when positively charged edges are placed adjacent to OCH_3 groups that donate electrons. It improves crystallinity and chemical stability by stabilizing the stacking COF layers.²⁹

1.3.4. Advantage of 2D layered structure over 3D network: Key role of 1D-nanochannel

2D layered Covalent Organic Frameworks (COFs) with 1D nanochannels offer distinct advantages over 3D network COFs, especially energy storage and conduction applications.³⁰ Their high surface area provides more active sites for charge storage, while the 1D-nanochannels facilitate fast ion diffusion, improving electrochemical performance. The well-defined electrode-electrolyte interface and ion confinement effects enhance energy storage capacity and stability. The tunable pore size allows for improved ion transport, and the flexibility and conductive properties of some COFs make them suitable for flexible energy

storage devices. The ease of exfoliation into thin films and the potential for functionalization offer opportunities for tailor-made materials in advanced energy storage technologies.^{31,32} The unique graphite-resembling layered morphology of 2D-COFs allows for the deliberate design of 1D-nanochannels, providing high predictability in their structure and properties governed due to accessibility of redox-active functional groups.³³ In contrast, the pores of 3D COFs are much less predictable due to their more complex and interpenetrated network structures. This ability to pre-design well-defined nanochannels in 2D-COFs makes them particularly advantageous for applications where controlled transport and confinement of molecules or ions are crucial, such as charge storage and conduction. Interestingly, the walls of the 1D channels can be decorated with various heteroatoms and redox-active functional groups to build a tailor-made interface. This interface provides the unique environment to trigger multiple interactions with the incoming guest-ions, which impacts the electrochemical activity of the 2D-COFs.³⁴⁻³⁷

AIM: The work constituting this thesis focuses on the engagement of the above-mentioned advantages of COFs in making electrodes, and proton conducting membranes for supercapacitors, metal-ion batteries, and fuel cells, which have the potential to revolutionize the alternate energy sector. This requires an overview of charge storage materials presented below.

1.4. Basic working principle of the energy applications; capacitor, battery, and fuel cell

Electrical energy storage and electrochemical energy conversion devices are essential in our daily lives, with broad applications in telecommunication devices (cell phones, tablets), standby power systems (laptops, cameras, and iPads), and electric transport vehicles, including heavy-duty vehicles. The energy source of capacitors, batteries, or fuel cells usually powers electronic devices at the circuit level. In the first two cases (capacitors, batteries), the stored energy generates an electric potential that drives a directional flow of electrons during charging or discharging, generating an electric current. This produced current can then power electrical devices connected within a circuit. Fuel cells, on the other hand, are an electrochemical energy conversion technology that directly transforms the chemical energy of a fuel and an oxidant into electrical energy. In order to fuel numerous electronic devices and ensure their effectiveness in modern lifestyles, these energy storage and conversion technologies are essential.³⁸

Capacitors, batteries, and fuel cells are energy storage devices classified based on two fundamental parameters: energy density and power density (Figure 1.5.).³⁹ Capacitors have

lower energy density as they store energy in an electrostatic field while offering exceptionally high-power density, making them suitable for delivering rapid bursts of power for short periods. Batteries provide higher energy density than capacitors as they store energy electrochemically but have moderate power density. They are well-suited for applications that require sustained power output. Fuel cells, on the other hand, boast the highest energy density among the three, generating electrical energy through electrochemical reactions.⁴⁰ While they have moderate power density, they deliver sustained and high-energy output over prolonged periods. The selection of the appropriate energy storage device depends on the explicit needs and demands of the application, with capacitors, batteries, and fuel cells offering distinct advantages for various use cases.⁴¹

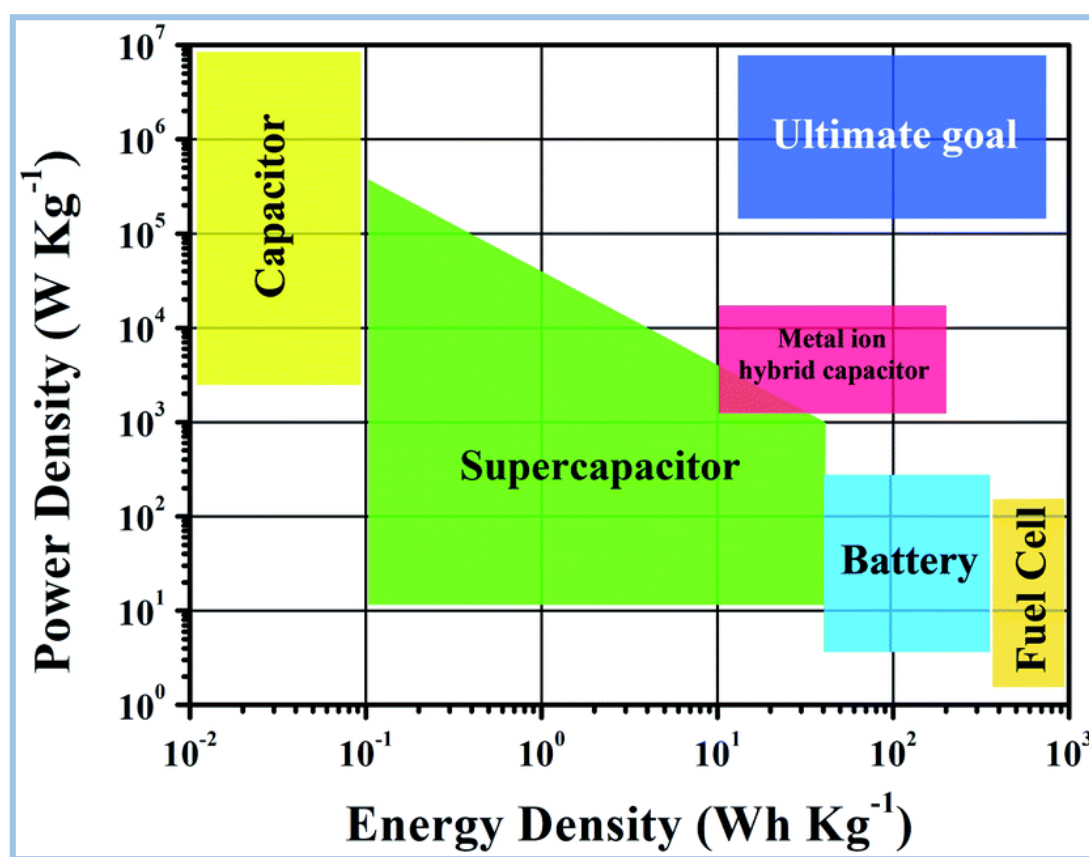


Figure 1.5. The Ragone plot shows the position of the battery, capacitor, and fuel cell in expression of energy density and power density (Adapted from ref. 41).

1.4.1. Supercapacitor:

Supercapacitors are a specialized type of capacitor that can store electrical charge much higher than ordinary capacitors. Unlike traditional capacitors, supercapacitors can undergo frequent

charge-discharge cycles even at high current levels. They occupy a unique position between capacitors and rechargeable batteries, offering a higher energy density than conventional ones. Supercapacitors have gained significant attention in research and development due to several advantageous characteristics.^{42,43} One key advantage is their higher power density, allowing them to deliver energy rapidly and effectively. Additionally, supercapacitors have lower maintenance costs, making them more cost-effective over a longer lifespan. They also exhibit a wide operating range, enabling their use in various environmental conditions without compromising performance. Furthermore, supercapacitors tend to have a longer cycle life, meaning they can undergo a significantly higher number of charge-discharge cycles before experiencing a decrease in performance.⁴⁴ These characteristics make supercapacitors

well-suited for applications that require high-power delivery, such as regenerative braking systems in electric vehicles, peak power support in renewable energy systems, and smoothing power fluctuations in electronic devices. As research and development progress, supercapacitors hold great potential to improve energy storage technologies further and contribute to more efficient and sustainable energy solutions.⁴⁵

1.4.1.1. Electric Double-Layer Capacitors (EDLCs):

Electric double layers are formed at the electrode-electrolyte interface in electrostatic double-layer (EDLC) or double-layer capacitors, which store electrical energy in this way. The porous electrodes develop a double layer when a voltage is applied because the electrolyte's ions build up on their surface. As shown in Figures 1.6 and 1.7, the physical adsorption and desorption of ions at the electrode surfaces result in unique curve characteristics for galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) measurements.⁴⁶ Fast and reversible charge-discharge cycles are made possible by this technology, producing a high power density. EDLCs are known for their long cycle life, low internal resistance, and excellent performance at high current densities. They are often used in applications that require rapid energy delivery, like regenerative braking systems in hybrid vehicles and power backup systems.⁴⁷

1.4.1.2. Pseudo-capacitors:

Pseudocapacitors, also known as redox supercapacitors, store energy through redox reactions at or near the electrode surface. Unlike EDLCs, pseudocapacitors involve faradaic charge storage, where a reversible redox reaction occurs between the electrode material and the

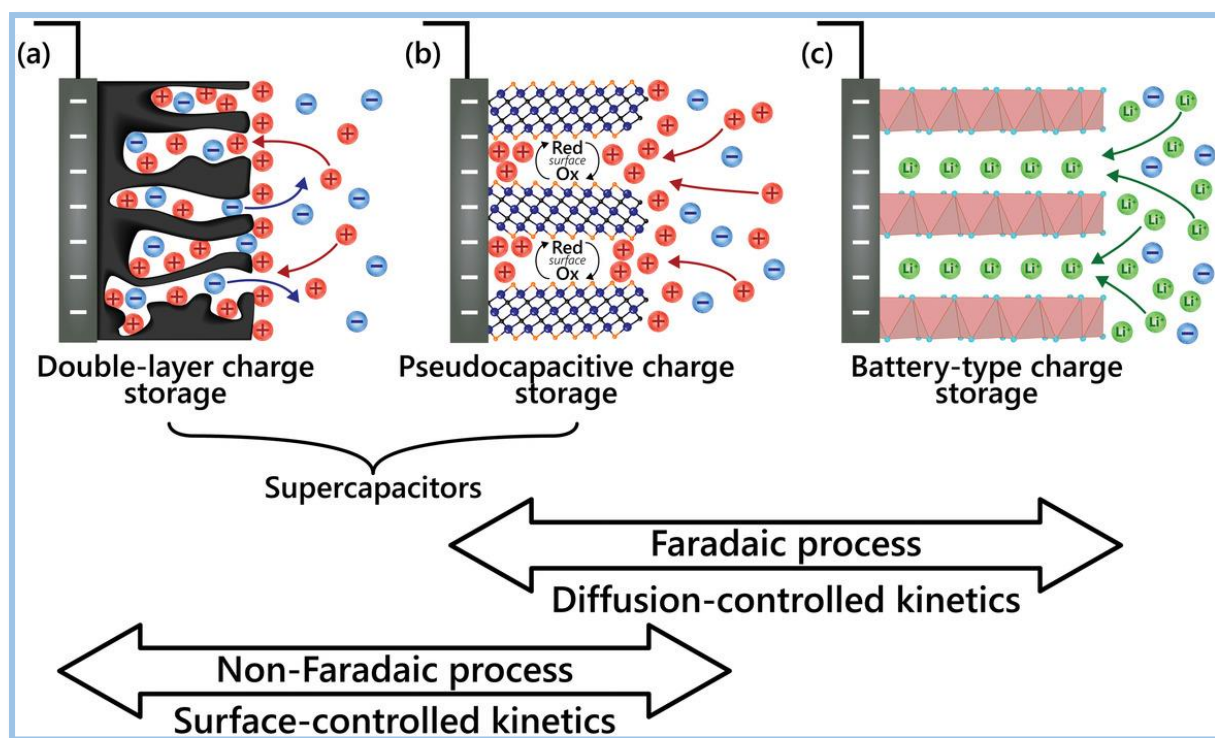


Figure 1.6. representation of the electrode processes occurring at a) electrical double-layer capacitive, b) pseudocapacitive, and c) faradaic electrodes (Adapted from ref. 46).

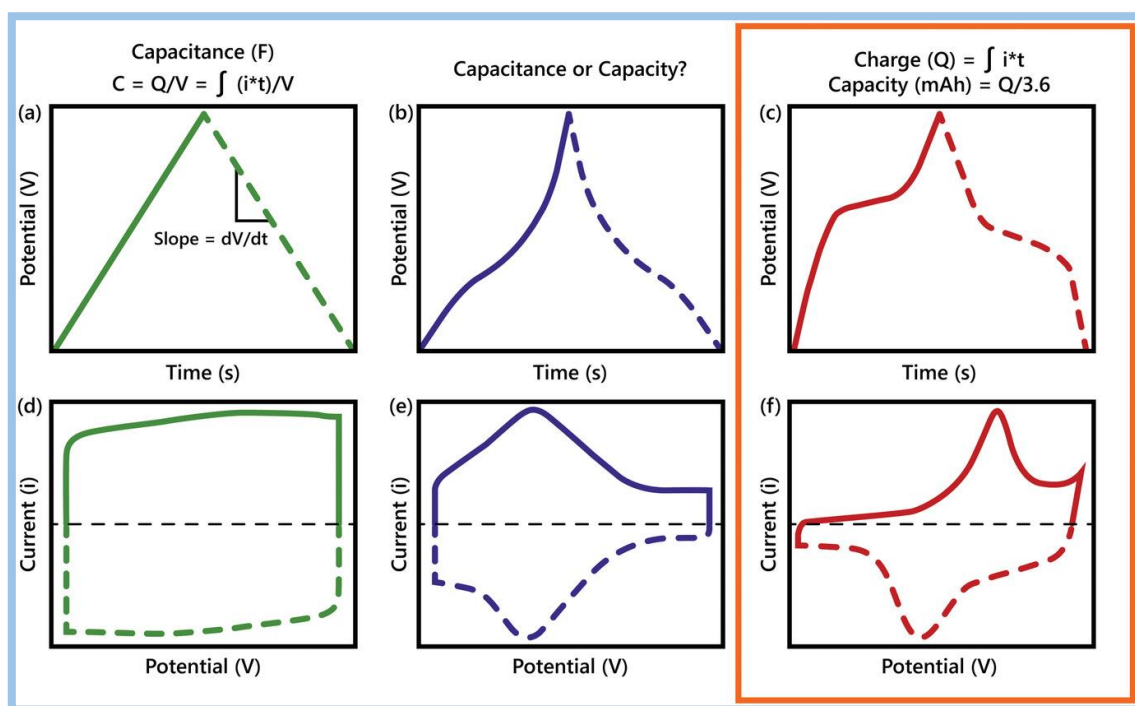


Figure 1.7. Representative electrical output feature of three different types of electrodes, including (a,d) electrical double layer. (b, e) pseudocapacitive. (c,f) battery type. (a–c) Schematic representation

of galvanostatic charge-discharge curves displaying linear as well as nonlinear responses with time and (d–f) CV profiles corresponding to galvanostatic charge-discharge. (Adapted from ref. 46)

electrolyte generating specific curve characteristic galvanostatic charge–discharge (GCD) and cyclic voltammetry (CV) (Figures 1.6. and 1.7.).⁴⁷ This redox reaction enables pseudocapacitors to store more energy per unit volume than EDLCs. Pseudocapacitors combine the fast charging-discharging capabilities of EDLCs with the higher energy storage capacity of batteries. They provide a middle ground between the power density of EDLCs and the energy density of batteries, making them suitable for applications that require both high-energy storage and fast power delivery.^{48,49}

1.4.2. Batteries:

Batteries are electrochemical energy storage devices that convert chemical energy into electrical energy. They are widely used in various applications, from powering small electronic devices to providing energy storage for electric vehicles and renewable energy systems.⁵⁰ The essential components of a battery include two electrodes (anode and cathode) separated by an electrolyte. During the charging process, a chemical reaction occurs at the electrodes, causing ions to move from one electrode to the other through the electrolyte (generating specific curve characteristic cyclic voltammetry (CV), and galvanostatic charge–discharge (GCD) (Figures 1.6. and 1.7.)). This process stores energy in the battery. When the battery is connected to an external circuit, such as a device or an electrical system, the stored energy is released as an electrical current, powering the connected load. Batteries come in various chemistries, each with unique characteristics, including energy density, power density, cycle life, and cost. Some common types of batteries include lead-acid, lithium-ion, nickel-metal hydride (NiMH), and zinc-ion batteries.⁵¹

1.4.3. Working Principle of Batteries:

The working principle of batteries involves converting chemical energy into electrical energy through electrochemical reactions. Batteries consist of three main components: anode and cathode and an electrolyte.^{52,53}

Anode: The anode represents the negative electrode of a battery. It is typically consisting of a reactive material that can release electrons during a chemical reaction.

Cathode: The cathode represents the positive electrode of a battery. It is typically consisting of a material that can accept electrons during a chemical reaction.

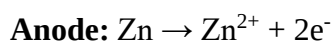
Electrolyte: Ionic flow between the anode and cathode is made possible by the electrolyte, which serves as a medium. Typically, it is a solid substance or an ion-conductive fluid.

1.4.3.1. Working of Zn ion Batteries: A Case Study

Like any rechargeable battery, Zinc-ion (Zn-ion) batteries use zinc ions as the charge carriers between the anode and cathode during the process of charge and discharge cycles. The working principle of Zn-ion batteries which requires the movement of zinc ions between the electrodes (cathode and anode) via the electrolyte, accompanied by redox reactions at each electrode (Figure 1.8.). Typically, the Zn metal strip is an anode, transition metal oxides or polyanions polymeric materials as cathode, and salts of Zn dissolved in the aqueous or nonaqueous solvents as electrolytes.⁵⁴⁻⁵⁶

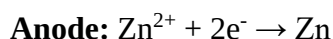
During discharging

During the discharge process (when the battery is being used to power a device, zinc undergoes an oxidation reaction, releasing two electrons ($2e^-$) and forming zinc ions. The cathode material undergoes a reduction reaction, capturing the zinc ions and electrons (external circuit) from the anode to form a compound with zinc.



During charging

When the Zn-ion battery is connected to an external power source for recharging, the redox reactions at the anode and cathode are reversed. Zinc ions (Zn^{2+}) are driven back to the anode, where they are reduced to form zinc metal (Zn), and the cathode material releases the captured electrons and zinc ions to revert to their original state.



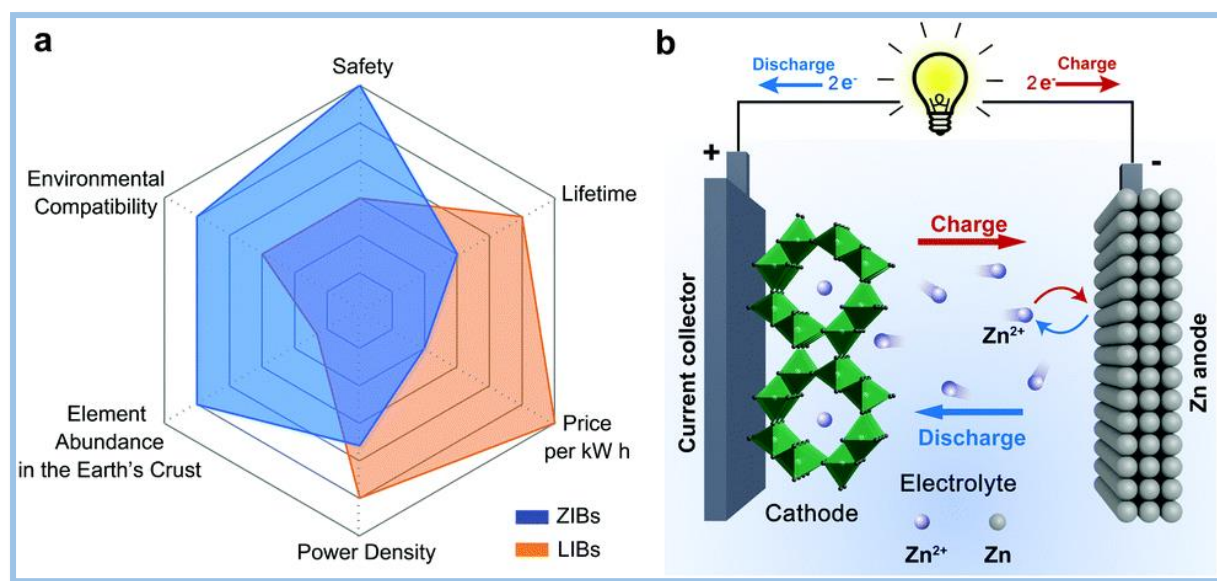


Figure 1.8. (a) Multi-angle comparison of lithium-ion and zinc-ion batteries. (b) Schematic representation of the working principle of rechargeable ZIBs (Adapted from ref. 57).

Their use of zinc as the charge carrier offers advantages in abundance, low cost, and environmental friendliness, and current research is focused on enhancing the performance and cycle life of Zn-ion batteries for practical applications.

1.4.4. Fuel Cells:

Fuel cells (FCs) are electrochemical devices that efficiently convert chemical energy from fuel and oxygen into electrical energy. They offer a promising alternative to conventional combustion-based power generation, as they can produce electricity with higher thermodynamic efficiencies and lower greenhouse gas emissions.⁵⁸ Fuel cells come in various configurations, depending on the type of fuel and electrolyte utilized, but they all share the same fundamental working principle. One widely used type of fuel cell is the Proton Exchange Membrane (PEM) fuel cell, which operates using hydrogen and a proton-conducting polymer electrolyte (Figure 1.9).⁵⁹ Fuel cells have emerged as a superior energy technology due to their multiple advantages. Their lightweight and compact configuration makes them highly suitable for portable and mobile applications. Operating at lower temperatures than traditional power generation techniques reduce heat losses and improves efficiency. Their non-corrosive nature ensures extended lifespans and reduced maintenance costs. Fuel cells can sustain high current densities, enabling rapid charge-discharge capabilities and quick response times. Notably, some fuel cell types, such as hydrogen fuel cells, offer fast refuelling options, rendered them

as a potential candidate for various practical applications such as in portable electronics, electric vehicles (EVs), and large-scale stationary power generation systems. Many companies, including Ballard Power Systems, Versa Power Systems, UTC Power Corporation, Toyota, Honda, and Mercedes-Benz, are actively commercializing fuel cell technologies, driving their adoption in various industries.

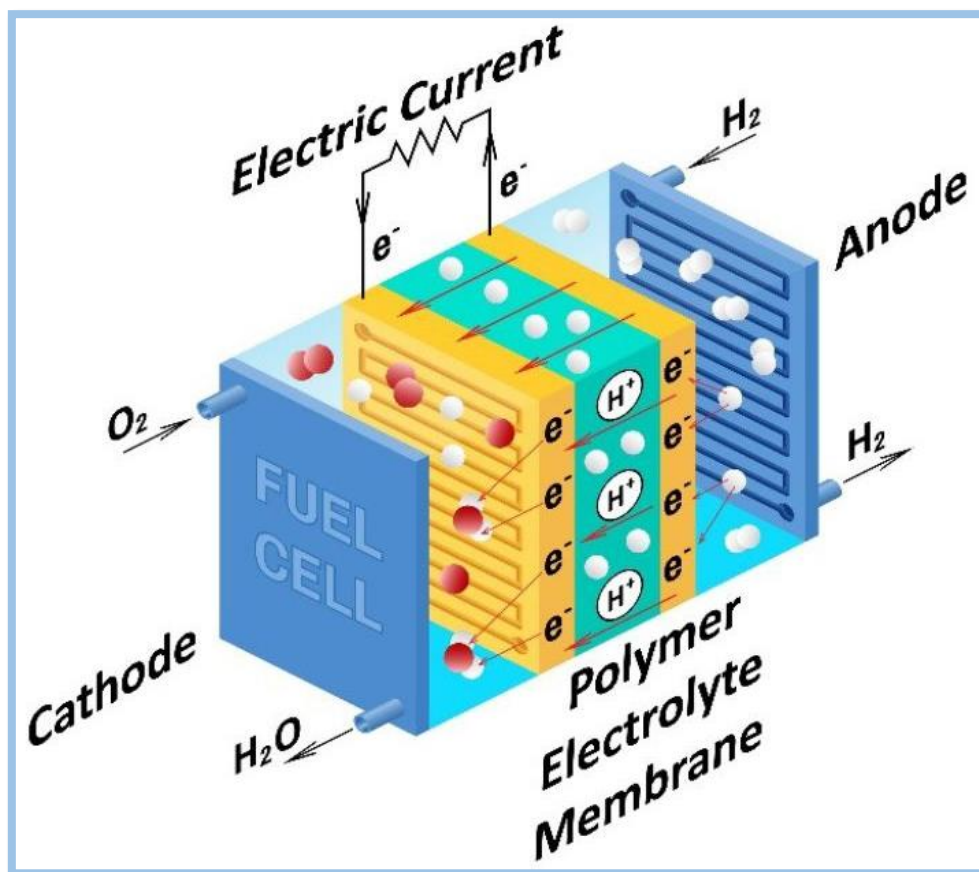


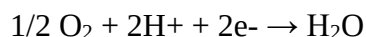
Figure1.9. A basic PEM fuel cell schematic representation. (Adapted from <https://ch.mathworks.com/discovery/fuel-cell-model.html>).

1.4.4.1. Working of Fuel Cells:

The core components of a PEM fuel cell are the two electrodes (anode and cathode) sandwiched with a proton-conducting polymer electrolyte membrane (Figure1.9.).⁵⁹ The overall chemical reaction that takes place in a hydrogen-oxygen PEM fuel cell can be represented as follows:

Anode (Oxidation reaction):



Cathode (Reduction reaction):**Overall Cell Reaction:**

At the anode, a platinum catalyst facilitates hydrogen atom splitting at the electrolyte, catalyst, and pore interface, generating electrons and protons. The polymer electrolyte membrane permits the transfer of protons, allowing them to move to the cathode. However, it restricts the movement of electrons, which are instead transported to the cathode through an external circuit. At the cathode, oxygen reacts with the protons received from the anode and electrons from the external circuit to produce water. In summary, fuel cells utilize hydrogen and oxygen to generate clean electricity as the primary product, with water being produced as a by-product of the electrochemical reactions.

Difference between capacitor batteries and fuel cells

Characteristic	Capacitor	Battery	Fuel Cell
Working Principle	Electrostatic energy storage	Chemical energy storage	Electrochemical energy generation
Energy Storage	Relatively lower energy density	Higher energy density	Highest energy density
Power Delivery	Very high power density	Moderate power density	Moderate power density
Energy Supply Duration	Short duration (rapid discharge)	Longer duration (steady output)	Longer duration (steady output)
Rechargeable	Yes, through electricity	Yes, through electricity	Yes, H ₂ supply needed
Environmental Impact	Often more environmentally friendly	Some types may contain toxins	Generally, more environmentally friendly
Applications	Camera flashes, quick electronic devices	Portable electronics, electric vehicles, backup power	Stationary and portable power generation

1.4.5. Redox-active polymers for metal ion-battery, supercapacitors, and fuel cells:

Redox-active polymers have appeared as reliable materials for use in metal-ion batteries, supercapacitors, and fuel cells. These polymers, crafted from well-selected monomeric units, can function as an effective electrode material offering enhanced charge storage and as membranes for fuel cells with higher ion conduction capabilities. Through the strategic integration of easily accessible redox-active functional groups on an atomic scale, these polymers achieve high storage capacities alongside stability under electrochemical conditions (Figure 1.10.).⁶⁰⁻⁶³ With an expanding synthetic repertoire and customizable properties such as their lightweight nature, design flexibility, and rapid kinetics, redox-active polymers emerge as an appealing contender for next-generation energy solutions. Continuous research and development endeavours are anticipated to further boost the performance and broaden their applications, driving their adoption across diverse industries.⁶⁴

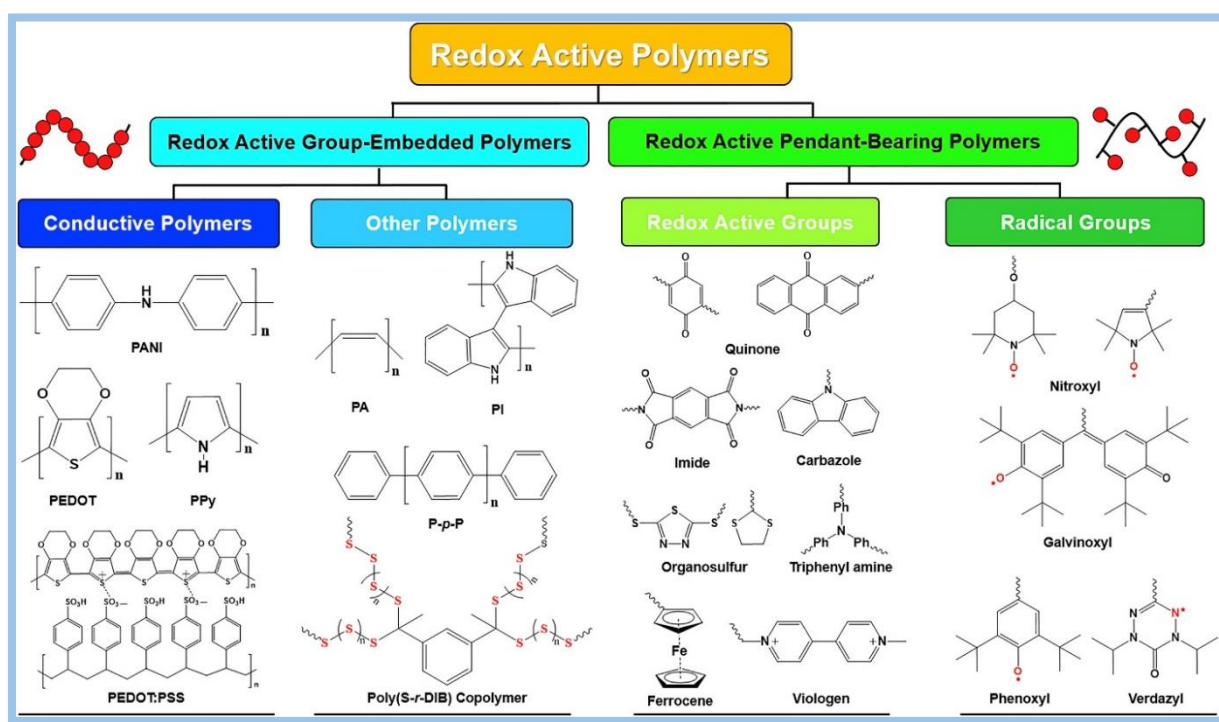


Figure1.10. Chemical Structure and Classification of Representative Redox-Active Polymers with Redox-Active Functional Groups (Adapted from ref. 64).

1.4.6. Recent literature on COFs for batteries, supercapacitors, and fuel cells:

COFs have rapidly gained traction in energy storage and proton conduction research. Their capacity to host redox-active groups, coupled with high surface area and tunable pore sizes, positions them as promising electrode materials for energy storage devices, including batteries, supercapacitors, and proton-conducting membranes.⁶⁵⁻⁶⁹

1.4.6.1. Recent literature on COF-based supercapacitors:

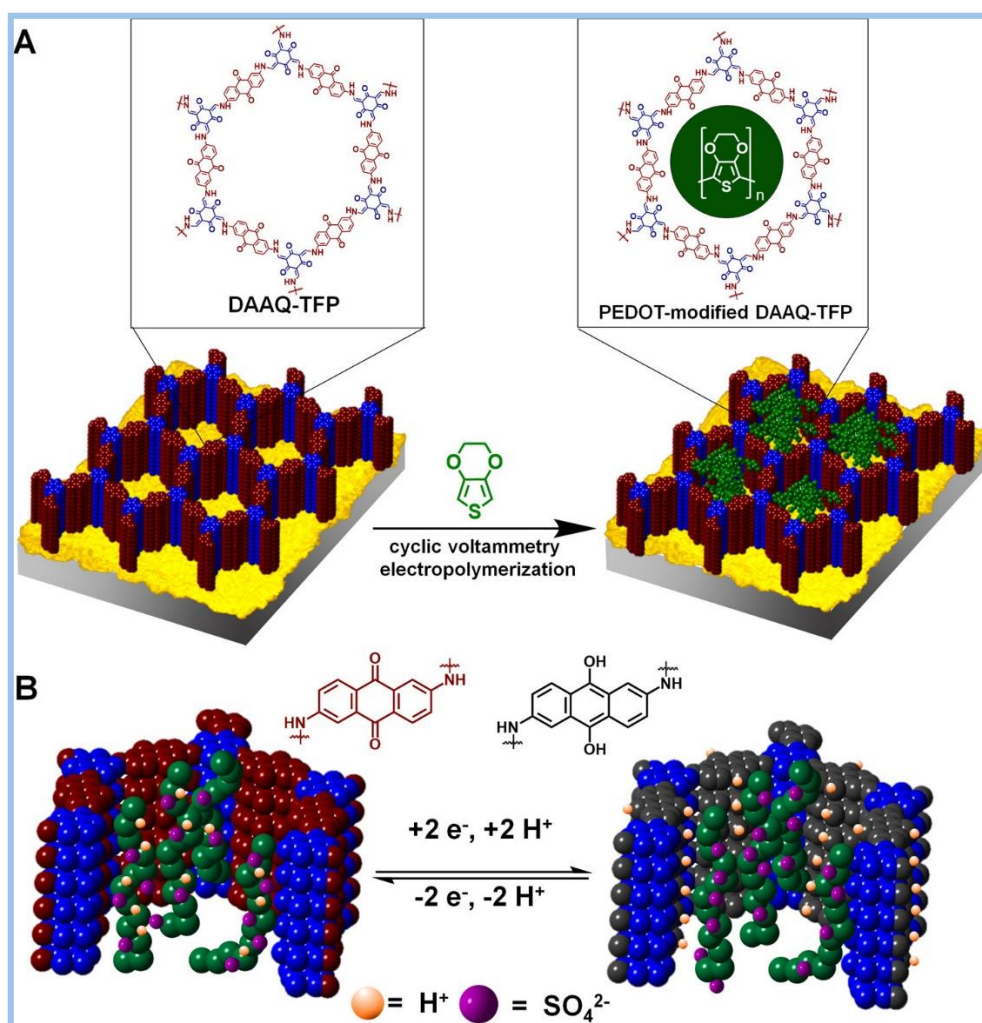


Figure 1.11.(A) Illustration of 3,4-ethylenedioxythiophene (EDOT) electro-polymerization and modification of DAAQ-TFP films, it illustrates hypothetically what might occur inside a COF crystallite. (B) Schematic representation of a cross-section of a pore during oxidation and reduction of the DAAQ functional groups (Adapted from ref. 70).

Mulzer et al. enhanced the electronic conductivity of a 2D COF film by incorporating poly(3,4-ethylenedioxythiophene) (PEDOT) within the pores through electropolymerization of 3,4-ethylenedioxythiophene (EDOT) and utilized for supercapacitor application. The resulting

PEDOT-intruded COF films exhibited significantly enhanced electrochemical conductivity, enabling efficient admittance to their redox-active groups. They also exhibited a 10-fold higher current than original films and maintained stable capacitances up to 10,000 cycles (Figure 1.11). This research particularly highlighted the potential of redox-active COFs for use in electrochemical energy storage (EES) devices by demonstrating higher volumetric energy and power densities similar to other porous carbon-based electrodes.⁷⁰

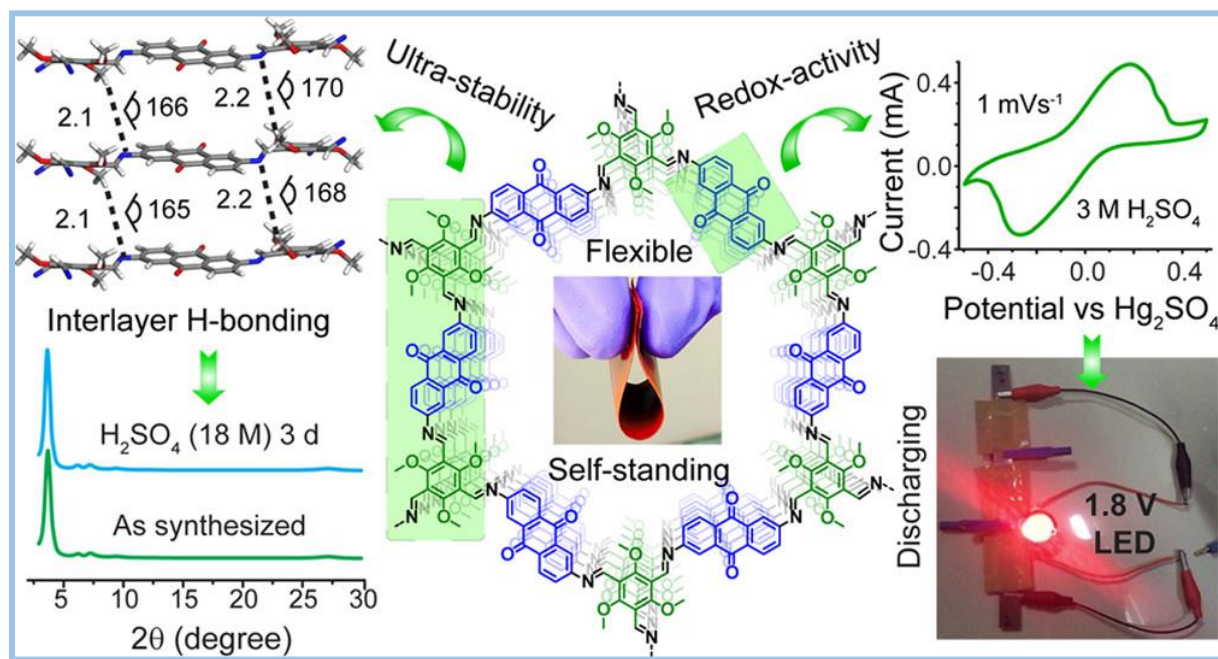


Figure 1.12. (A) Depiction of ultra-stability and redox activity introduced in COF with anthraquinone and tri-methoxy functional group, utilized for supercapacitor application (Adapted from ref. 71).

Later Halder et al. successfully synthesized a redox-active and chemically robust covalent organic framework (COF) for demonstration as a self-standing electrode for supercapacitors. The remarkable chemical robustness of the COF is ascribed to the integrated effects of steric hindrance and hydrophobic shield of C=N (imine) bonds by adjacent -OCH_3 functional group and interlayer C—H $\cdots$ N hydrogen bonding. Additionally, the material displays a remarkable areal capacitance, where the stored energy is believed to be a combination of electrical double-layer capacitance (EDLC) and pseudocapacitive behavior, due to the porosity nature and redox interconversion between quinone and hydroquinone moieties, respectively (Figure 1.12.). The COF's robust chemical nature allowed for electrochemical studies using 2 M aqueous H_2SO_4 /PVA gel, revealing a long cyclic life of over 50,000 cycles with 65% capacitance retention with solid-state device.⁷¹

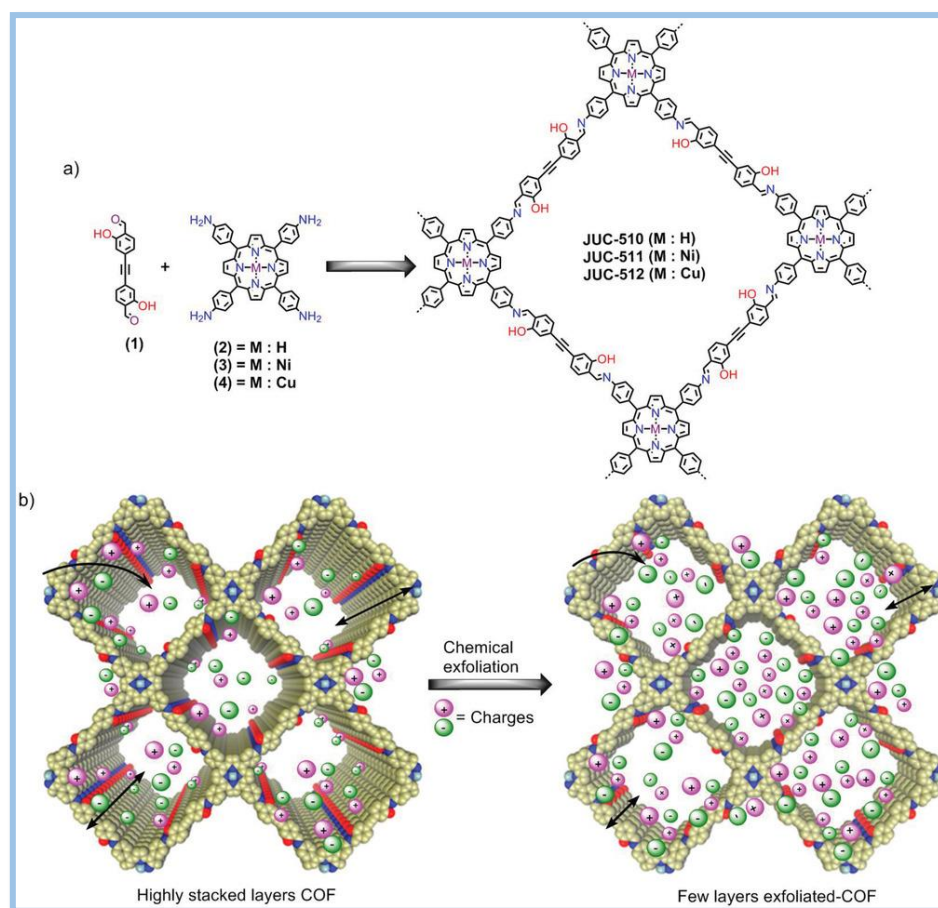


Figure 1.13. (a) Synthesis of JUC-510 COF, JUC-511 COF, and JUC-512 COF; and (b) The illustration shows the behavior of charge storage using COFs and exfoliated COFs (e-COFs). (Adapted from ref. 72).

Yusran et al. present a bunch of capacitors based on with and without exfoliated COFs capable of excellent double-layer charge storage. Due to its superior power density and extended cycle life in comparison to batteries and pseudocapacitors, double-layer capacitors are popular as energy storage devices. The mesoporous 2D COFs used in this study possess an eclipsed structure with AA layer-stack and 3.4 nm square-type pore, providing BET surface area up to $1170 \text{ m}^2 \text{ g}^{-1}$ (Figure 1.13), and exhibiting high chemical and thermal robustness. A scalable, facile, and mild chemical exfoliation technique was utilized to exfoliate the COFs, resulting in thin-layer structures with an approximately 22 nm average thickness. The exfoliate-COF-based capacitor coin cells demonstrated impressive performance metrics, including high areal capacitance of 5.46 mF cm^{-2} at $1,000 \text{ mV s}^{-1}$. It exhibits nearly ideal double-layer charge storage behavior, even at $30,000 \text{ mV s}^{-1}$ charge-discharge rates, and the maintenance of nearly 100% capacitance retention upto 10,000 cycles. Overall, this study sheds light on the potential

application of COF materials for enhancing the performance of electrochemical double-layer capacitors (EDLCs).⁷²

1.4.6.2. Recent literature on COF-based Zn ion battery:

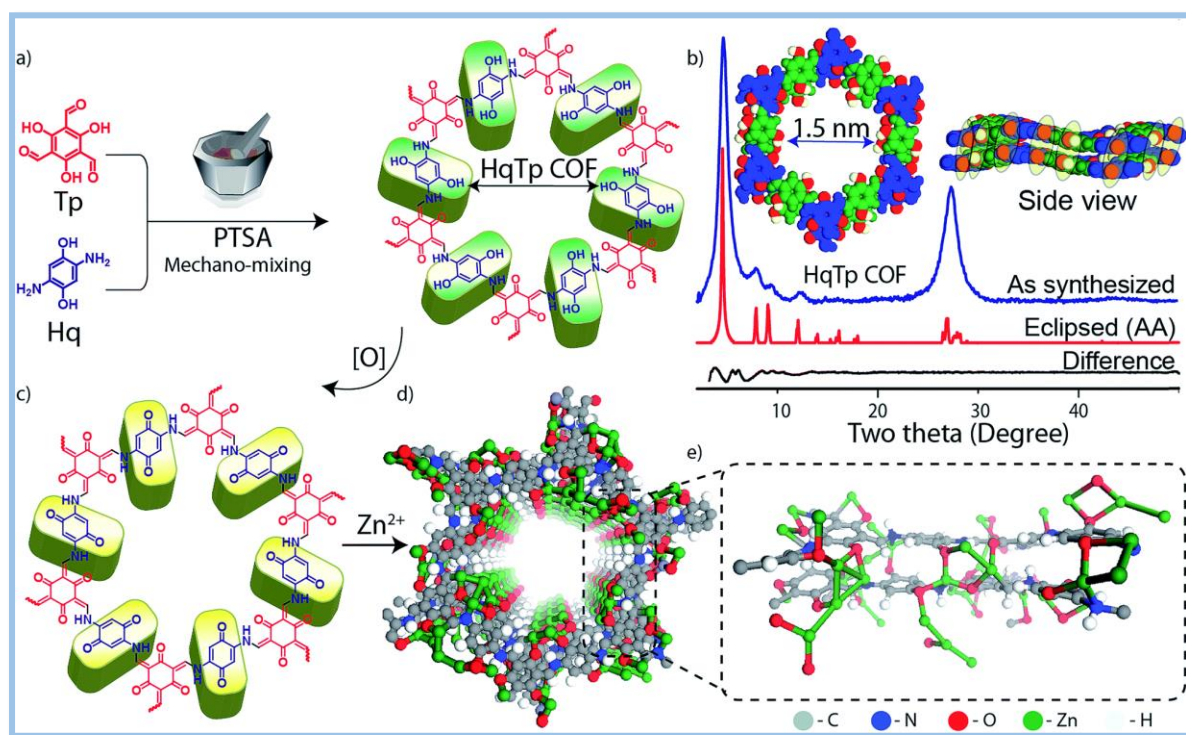


Figure 1.14. (a) Schematic representation of the HqTp COF. (b) PXRD pattern using the slipped SCC-DFT model in the AA eclipsed mode. (c) The hydroquinone to quinone transformation in HqTp COF by electrochemical oxidation. (d and e) The DFTB model represent the interaction of Zn^{2+} ions with the surrounding layers of HqTp COF. (Adapted from ref. 73)

Khayum et al. successfully demonstrated hydroquinone-based HqTp COF as a novel cathode material for rechargeable aqueous ZIBs. The HqTp COF exhibits rich functional groups capable of efficiently chelation of Zn^{2+} cations. The strong interaction between the Zn^{2+} cations and the C=O and N–H groups from the adjacent layers results in a good specific capacity of 276 mA h g^{-1} at 125 mA g^{-1} (Figure 1.14.). We presume that utilizing COFs as organic cathodes in such devices paves the way for developing even more potent crystalline polymeric organic cathodes in the imminent.⁷³ This research represents a substantial step forward in the advancement of high-performance energy storage materials for rechargeable

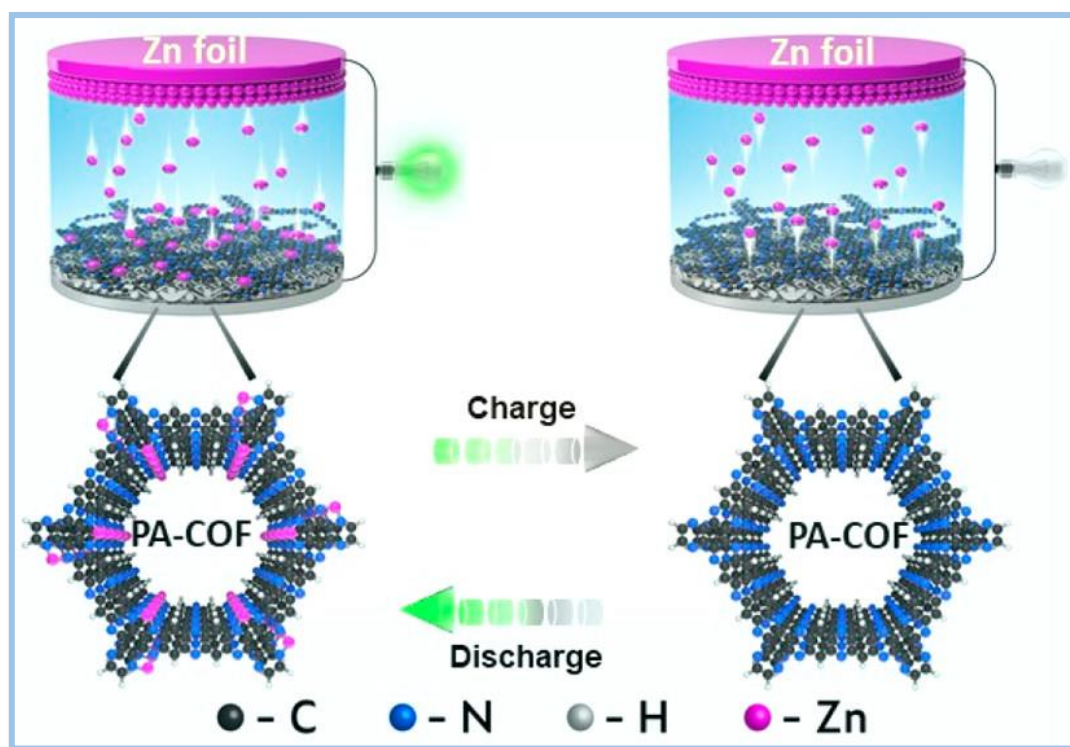


Figure 1.15. a) Schematic representation of zinc ion super-capattery and electrochemical performance of ZIS setup as PA-COF||1.0 M ZnSO₄||Zn metal with 1.0 M ZnSO₄ electrolyte (Adapted from ref. 74)

batteries. Latter Wang et al. have synthesized a novel phenanthroline-based COF and investigated its potential as a cathode for the aqueous zinc ion supercapattery. The PA-COF exhibited a remarkably high capacity of 247 mAh g⁻¹ at 0.1 A g⁻¹ current density (Figure 1.15.). The COF cathode's excellent cyclic stability was even more impressive, with a 0.38% average capacity decay over each cycle during 10,000 cycles at a higher current density of 1.0 A g⁻¹. Moreover, experimental investigation and theoretical simulations revealed that the phenanthroline moieties within the PA-COF served as the active ion-binding site, further enhancing its electrochemical performance.⁷⁴ The success of the nitrogen-rich COF design strategy represents a significant advancement and opens up a promising avenue for applying COF electrodes in aqueous ion batteries.

1.4.6.1. Recent literature on COF-based membrane for fuel cell application:

Yang et al. developed a stepwise synthesis strategy to synthesize covalent organic frameworks (COFs) with various bond linkages, resulting in a series of stable COFs named NKCOFs. These NKCOFs were enriched with ample proton-accepting and donating groups.

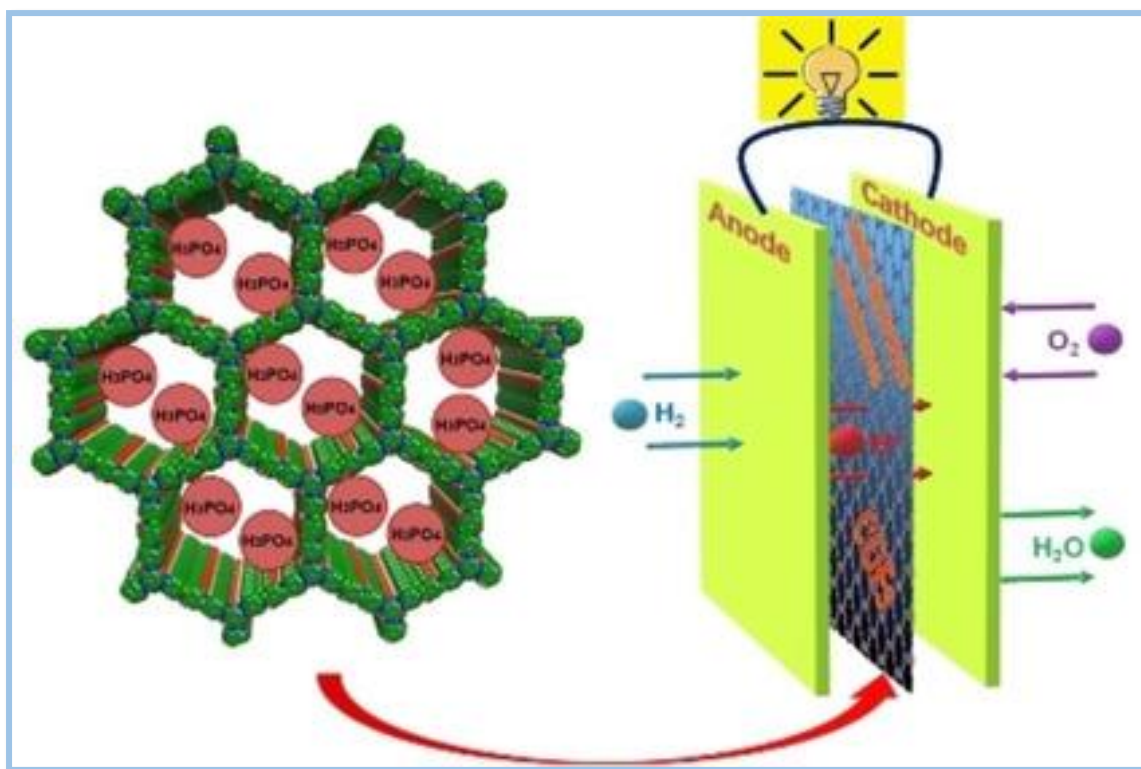


Figure1.16. H_3PO_4 loaded COF as $\text{H}_3\text{PO}_4@\text{NKCOF-1}$ and Scheme of the fuel cells with MEA of $\text{H}_3\text{PO}_4@\text{NKCOFs}$ solid electrolyte membranes (Adapted from ref. 75).

They exhibited high crystallinity, surface areas, and remarkable stability under various harsh conditions, including exposure to organic solvents, boiling water, and strong acids or bases. When NKCOFs were loaded with H_3PO_4 (forming $\text{H}_3\text{PO}_4@\text{NKCOFs}$), they exhibited high proton conductivity of $1.13 \times 10^{-1} \text{ S cm}^{-1}$ at 80°C under 98 % relative humidity (Figure1.16.). Moreover, the authors successfully fabricated membranes for electrode assemblies as proton exchange membrane (PEM) fuel cells. Particularly, $\text{H}_3\text{PO}_4@\text{NKCOF-1}$ demonstrated remarkable performance, with current and power densities of 456 mA cm^{-2} , and 81 mW cm^{-2} , respectively. This research offers crucial insights into the design of multifunctional COFs, and the reported synthesis strategy holds broad applicability, potentially extending to other COF systems. Additionally, this study achieves high protonic conductivity and presents the best performance of PEM fuel cells.⁷⁵

1.5. References:

- [1] Gartner T. E.; III; Jayaraman, A., Modeling and Simulations of Polymers: A Roadmap. *Macromolecules* **2019**, 52 (3), 755-786.
- [2] Park, S.; Shou, W.; Makatura, L.; Matusik, W.; Fu, K. K., 3D printing of polymer composites: Materials, processes, and applications. *Matter* **2022**, 5 (1), 43-76.
- [3] Schlüter, A. D., Features that make macromolecules 2D polymers. *React Funct Polym.* **2021**, 161, 104856.
- [4] Samir, A.; Ashour, F. H.; Hakim, A. A.; Bassyouni, M., Recent advances in biodegradable polymers for sustainable applications. *Npj Materials Degradation* **2022**, 6 (1), 68.
- [5] Wu, J.; Xu, F.; Li, S.; Ma, P.; Zhang, X.; Liu, Q.; Fu, R.; Wu, D., Porous polymers as multifunctional material platforms toward task-specific applications. *Adv. Mater.* **2019**, 31 (4), 1802922.
- [6] Bandyopadhyay, S.; Anil, A. G.; James, A.; Patra, A., Multifunctional porous organic polymers: tuning of porosity, CO₂, and H₂ storage and visible-light-driven photocatalysis. *ACS Appl Mater Interfaces* **2016**, 8 (41), 27669-27678.
- [7] Chakraborty, D.; Nandi, S.; Sinnwell, M. A.; Liu, J.; Kushwaha, R.; Thallapally, P. K.; Vaidhyanathan, R., Hyper-cross-linked porous organic frameworks with ultramicropores for selective xenon capture. *ACS Appl Mater Interfaces* **2019**, 11 (14), 13279-13284.
- [8] Mohamed, M. G.; EL-Mahdy, A. F.; Kotp, M. G.; Kuo, S.-W., Advances in porous organic polymers: Syntheses, structures, and diverse applications. *Mater. Adv.* **2022**, 3 (2), 707-733.
- [9] Das, S.; Heasman, P.; Ben, T.; Qiu, S., Porous organic materials: strategic design and structure–function correlation. *Chem. Rev.* **2017**, 117 (3), 1515-1563.
- [10] Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M., Porous, crystalline, covalent organic frameworks. *science* **2005**, 310 (5751), 1166-1170.
- [11] Alahakoon, S. B.; Diwakara, S. D.; Thompson, C. M.; Smaldone, R. A., Supramolecular design in 2D covalent organic frameworks. *Chem. Soc. Rev.* **2020**, 49 (5), 1344-1356.
- [12] Jin, S.; Allam, O.; Jang, S. S.; Lee, S. W., Covalent organic frameworks: Design and applications in electrochemical energy storage devices. *InfoMat* **2022**, 4 (6), e12277.
- [13] Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D., Covalent organic frameworks: design, synthesis, and functions. *Chem. Rev.* **2020**, 120 (16), 8814-8933.
- [14] Chen, X.; Geng, K.; Liu, R.; Tan, K. T.; Gong, Y.; Li, Z.; Tao, S.; Jiang, Q.; Jiang, D., Covalent organic frameworks: chemical approaches to designer structures and built-in functions. *Angew. Chem., Int. Ed.* **2020**, 59 (13), 5050-5091.

- [15] Song, Y.; Sun, Q.; Aguila, B.; Ma, S., Opportunities of covalent organic frameworks for advanced applications. *Adv. Sci* **2019**, 6 (2), 1801410.
- [16] Abuzeid, H. R.; EL-Mahdy, A. F.; Kuo, S.-W., Covalent organic frameworks: Design principles, synthetic strategies, and diverse applications. *Giant* **2021**, 6, 100054.
- [17] Zhao, X.; Pachfule, P.; Thomas, A., Covalent organic frameworks (COFs) for electrochemical applications. *Chem. Soc. Rev.* **2021**, 50 (12), 6871-6913.
- [18] Guan, X.; Chen, F.; Fang, Q.; Qiu, S., Design and applications of three dimensional covalent organic frameworks. *Chem. Soc. Rev.* **2020**, 49 (5), 1357-1384.
- [19] Segura, J. L.; Royuela, S.; Ramos, M. M., Post-synthetic modification of covalent organic frameworks. *Chem. Soc. Rev.* **2019**, 48 (14), 3903-3945.
- [20] Sharma, R. K.; Yadav, P.; Yadav, M.; Gupta, R.; Rana, P.; Srivastava, A.; Zbořil, R.; Varma, R. S.; Antonietti, M.; Gawande, M. B., Recent development of covalent organic frameworks (COFs): synthesis and catalytic (organic-electro-photo) applications. *Mater. Horiz.* **2020**, 7 (2), 411-454.
- [21] Liu, X.; Huang, D.; Lai, C.; Zeng, G.; Qin, L.; Wang, H.; Yi, H.; Li, B.; Liu, S.; Zhang, M., Recent advances in covalent organic frameworks (COFs) as a smart sensing material. *Chem. Soc. Rev.* **2019**, 48 (20), 5266-5302.
- [22] Lanni, L. M.; Tilford, R. W.; Bharathy, M.; Lavigne, J. J., Enhanced hydrolytic stability of self-assembling alkylated two-dimensional covalent organic frameworks. *J. Am. Chem. Soc.* **2011**, 133 (35), 13975-13983.
- [23] Kandambeth, S.; Dey, K.; Banerjee, R., Covalent organic frameworks: chemistry beyond the structure. *J. Am. Chem. Soc.* **2018**, 141 (5), 1807-1822.
- [24] Janica, I.; Patroniak, V.; Samorì, P.; Ciesielski, A., Imine-Based Architectures at Surfaces and Interfaces: From Self-Assembly to Dynamic Covalent Chemistry in 2D. *Chem. Asian J.* **2018**, 13 (5), 465-481.
- [25] Guan, Q.; Zhou, L.-L.; Dong, Y.-B., Construction of Covalent Organic Frameworks via Multicomponent Reactions. *J. Am. Chem. Soc.* **2023**, 145 (3), 1475-1496.
- [26] Ma, T.; Kapustin, E. A.; Yin, S. X.; Liang, L.; Zhou, Z.; Niu, J.; Li, L.-H.; Wang, Y.; Su, J.; Li, J., Single-crystal x-ray diffraction structures of covalent organic frameworks. *Science* **2018**, 361 (6397), 48-52.
- [27] Li, X.; Cai, S.; Sun, B.; Yang, C.; Zhang, J.; Liu, Y., Chemically robust covalent organic frameworks: progress and perspective. *Matter* **2020**, 3 (5), 1507-1540.
- [28] Kandambeth, S.; Shinde, D. B.; Panda, M. K.; Lukose, B.; Heine, T.; Banerjee, R., Enhancement of chemical stability and crystallinity in porphyrin-containing covalent organic frameworks by intramolecular hydrogen bonds. *Angew. Chem. Int. Ed.* **2013**, 125 (49), 13290-13294.

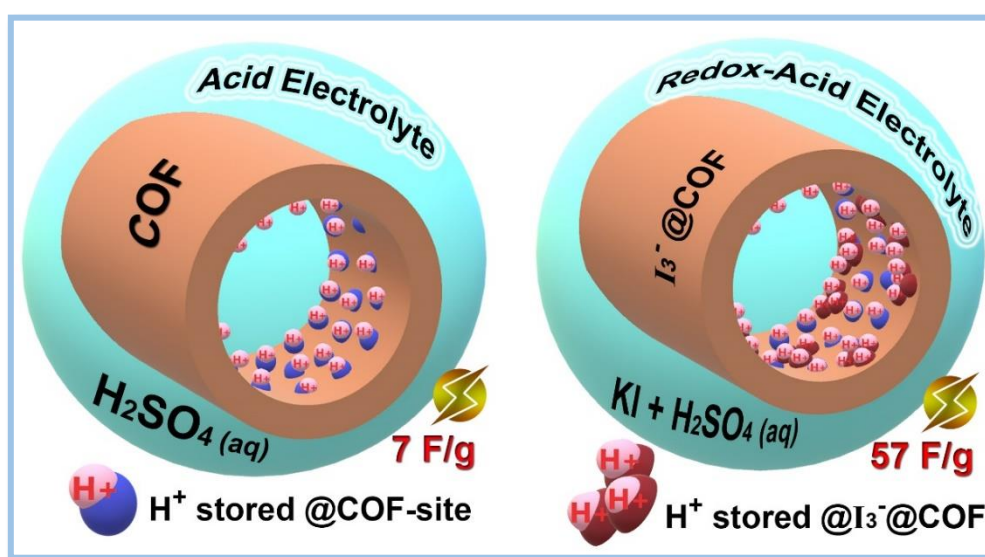
- [29] Xu, H.; Gao, J.; Jiang, D., Stable, crystalline, porous, covalent organic frameworks as a platform for chiral organocatalysts. *Nat. Chem.* **2015**, 7 (11), 905-912.
- [30] Ma, X.; Scott, T. F., Approaches and challenges in the synthesis of three-dimensional covalent-organic frameworks. *Commun. Chem* **2018**, 1 (1), 98.
- [31] Haldar, S.; Roy, K.; Nandi, S.; Chakraborty, D.; Puthusseri, D.; Gawli, Y.; Ogale, S.; Vaidhyanathan, R., High and reversible lithium-ion storage in self-exfoliated triazole-triformyl phloroglucinol-based covalent organic nanosheets. *Adv. Energy Mater.* **2018**, 8 (8), 1702170.
- [32] Haldar, S.; Roy, K.; Kushwaha, R.; Ogale, S.; Vaidhyanathan, R., Chemical exfoliation as a controlled route to enhance the anodic performance of COF in LIB. *Adv. Energy Mater.* **2019**, 9 (48), 1902428.
- [33] Li, X.; Yadav, P.; Loh, K. P., Function-oriented synthesis of two-dimensional (2D) covalent organic frameworks—from 3D solids to 2D sheets. *Chem. Soc. Rev.* **2020**, 49 (14), 4835-4866.
- [34] Dogru, M.; Bein, T., On the road towards electroactive covalent organic frameworks. *ChemComm* **2014**, 50 (42), 5531-5546.
- [35] Vudhichai Parasuk, and Donglin Jiang Ding, X.; Chen, L.; Honsho, Y.; Feng, X.; Saengsawang, O.; Guo, J.; Saeki, A.; Seki, S.; Irle, S.; Nagase, S.; Parasuk, V.; Jiang, D., An n-channel two-dimensional covalent organic framework. *J. Am. Chem. Soc.* **2011**, 133 (37), 14510-14513.
- [36] Mandal, A. K.; Mahmood, J.; Baek, J. B., Two-dimensional covalent organic frameworks for optoelectronics and energy storage. *ChemNanoMat* **2017**, 3 (6), 373-391.
- [37] Haug, W. K.; Moscarello, E. M.; Wolfson, E. R.; McGrier, P. L., The luminescent and photophysical properties of covalent organic frameworks. *Chem. Soc. Rev.* **2020**, 49 (3), 839-864.
- [38] Venkatesan, S. V.; Nandy, A.; Karan, K.; Larter, S. R.; Thangadurai, V., Recent advances in the unconventional design of electrochemical energy storage and conversion devices. *Electrochem. Energy Rev.* **2022**, 5 (4), 16.
- [39] Winter, M.; Brodd, R. J., What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* **2004**, 104 (10), 4245-4270.
- [40] Dutta, A.; Mitra, S.; Basak, M.; Banerjee, T., A comprehensive review on batteries and supercapacitors: development and challenges since their inception. *Energy Storage* **2023**, 5 (1), e339..
- [41] Liu, Y.; Wu, Q.; Liu, L.; Manasa, P.; Kang, L.; Ran, F., Vanadium nitride for aqueous supercapacitors: a topic review. *J. Mater. Chem. A* **2020**, 8 (17), 8218-8233.
- [42] Afif, A.; Rahman, S. M.; Azad, A. T.; Zaini, J.; Islan, M. A.; Azad, A. K., Advanced materials and technologies for hybrid supercapacitors for energy storage—A review. *J. Energy Storage* **2019**, 25, 100852.
- [43] Qi, J.; Yan, Y.; Cai, Y.; Cao, J.; Feng, J., Nanoarchitected design of vertical-standing arrays for supercapacitors: progress, challenges, and perspectives. *Adv. Funct. Mater.* **2021**, 31 (3), 2006030.

- [44] Zhang, S.; Pan, N., Supercapacitors performance evaluation. *Adv. Energy Mater.* **2015**, 5 (6), 1401401.
- [45] Yan, J.; Wang, Q.; Wei, T.; Fan, Z., Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. *Adv. Energy Mater.* **2014**, 4 (4), 1300816.
- [46] Mathis, T. S.; Kurra, N.; Wang, X.; Pinto, D.; Simon, P.; Gogotsi, Y., Energy storage data reporting in perspective—guidelines for interpreting the performance of electrochemical energy storage systems. *Adv. Energy Mater.* **2019**, 9 (39), 1902007.
- [47] Jiang, Y.; Liu, J., Definitions of pseudocapacitive materials: a brief review. *Energy Environ. Mater.* **2019**, 2 (1), 30-37.
- [48] Eftekhari, A., The mechanism of ultrafast supercapacitors. *J. Mater. Chem. A* **2018**, 6 (7), 2866-2876.
- [49] Zhong, C.; Deng, Y.; Hu, W.; Qiao, J.; Zhang, L.; Zhang, J., A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chem. Soc. Rev.* **2015**, 44 (21), 7484-7539.
- [50] Liang, Y.; Zhao, C. Z.; Yuan, H.; Chen, Y.; Zhang, W.; Huang, J. Q.; Yu, D.; Liu, Y.; Titirici, M. M.; Chueh, Y. L., A review of rechargeable batteries for portable electronic devices. *InfoMat* **2019**, 1 (1), 6-32.
- [51] Tian, Y.; Zeng, G.; Rutt, A.; Shi, T.; Kim, H.; Wang, J.; Koettgen, J.; Sun, Y.; Ouyang, B.; Chen, T.; Lun, Z.; Rong, Z.; Persson, K.; Ceder, G., Promises and challenges of next-generation “beyond Li-ion” batteries for electric vehicles and grid decarbonization. *Chem. Rev.* **2020**, 121 (3), 1623-1669.
- [52] Foreman, E.; Zakri, W.; Hossein Sanatimoghaddam, M.; Modjtahedi, A.; Pathak, S.; Kashkooli, A. G.; Garafolo, N. G.; Farhad, S., A review of inactive materials and components of flexible lithium-ion batteries. *Adv. Sustainable Syst.* **2017**, 1 (11), 1700061.
- [53] Kim, T.; Song, W.; Son, D.-Y.; Ono, L. K.; Qi, Y., Lithium-ion batteries: outlook on present, future, and hybridized technologies. *J. Mater. Chem. A* **2019**, 7 (7), 2942-2964.
- [54] Jia, X.; Liu, C.; Neale, Z. G.; Yang, J.; Cao, G., Active materials for aqueous zinc ion batteries: synthesis, crystal structure, morphology, and electrochemistry. *Chem. Rev.* **2020**, 120 (15), 7795-7866.
- [55] Zhang, X.; Hu, J. P.; Fu, N.; Zhou, W. B.; Liu, B.; Deng, Q.; Wu, X. W., Comprehensive review on zinc-ion battery anode: challenges and strategies. *InfoMat* **2022**, 4 (7), e12306.
- [56] Zhang, T.; Tang, Y.; Guo, S.; Cao, X.; Pan, A.; Fang, G.; Zhou, J.; Liang, S., Fundamentals and perspectives in developing zinc-ion battery electrolytes: a comprehensive review. *Energy Environ. Sci.* **2020**, 13 (12), 4625-4665.
- [57] Zhang, N.; Chen, X.; Yu, M.; Niu, Z.; Cheng, F.; Chen, J., Materials chemistry for rechargeable zinc-ion batteries. *Chem. Soc. Rev.* **2020**, 49 (13), 4203-4219.
- [58] Hussain, S.; Yangping, L., Review of solid oxide fuel cell materials: Cathode, anode, and electrolyte. *Energy Transitions* **2020**, 4, 113-126.

- [59] Seeberger, D.; Hartert, A.; Mayerhöfer, B.; Thiele, S., Bipolar-Interface Hydrogen Fuel Cells: A Review and Perspective on Future High-Performance, Low Platinum-Group Metal Content Designs. *ChemElectroChem* **2021**, *8* (8), 1430-1447.
- [60] Wang, A.; Tan, R.; Breakwell, C.; Wei, X.; Fan, Z.; Ye, C.; Malpass-Evans, R.; Liu, T.; Zwijnenburg, M. A.; Jelfs, K. E.; McKeown, N. B.; Chen, J.; Song, Q., Solution-processable redox-active polymers of intrinsic microporosity for electrochemical energy storage. *J. Am. Chem. Soc.* **2022**, *144* (37), 17198-17208.
- [61] Zhang, Q.; Dou, Y.; He, Q.; Deng, S.; Huang, Q.; Huang, S.; Yang, Y., Emerging Carbonyl Polymers as Sustainable Electrode Materials for Lithium-Free Metal-Ion Batteries. *Energy Environ. Mater.* **2022**, *5* (4), 1037-1059.
- [62] Abdel Maksoud, M.; Fahim, R. A.; Shalan, A. E.; Abd Elkodous, M.; Olojede, S.; Osman, A. I.; Farrell, C.; Al-Muhtaseb, A. a. H.; Awed, A.; Ashour, A., Advanced materials and technologies for supercapacitors used in energy conversion and storage: a review. *Environ Chem Lett* **2021**, *19*, 375-439.
- [63] Rohland, P.; Schröter, E.; Nolte, O.; Newkome, G. R.; Hager, M. D.; Schubert, U. S., Redox-active polymers: The magic key towards energy storage—a polymer design guideline progress in polymer science. *Polym. Sci.* **2022**, *125*, 101474.
- [64] Kim, J.; Kim, J. H.; Ariga, K., Redox-active polymers for energy storage nanoarchitectonics. *Joule* **2017**, *1* (4), 739-768.
- [65] Kandambeth, S.; Kale, V. S.; Shekhah, O.; Alshareef, H. N.; Eddaoudi, M., 2D covalent-organic framework electrodes for supercapacitors and rechargeable metal-ion batteries. *Adv. Energy Mater.* **2022**, *12* (4), 2100177.
- [66] Dutta, S.; Bhaumik, A.; Wu, K. C.-W., Hierarchically porous carbon derived from polymers and biomass: effect of interconnected pores on energy applications. *Energy Environ. Sci.* **2014**, *7* (11), 3574-3592.
- [67] Wang, M.; Guo, H.; Xue, R.; Li, Q.; Liu, H.; Wu, N.; Yao, W.; Yang, W., Covalent organic frameworks: A new class of porous organic frameworks for supercapacitor electrodes. *ChemElectroChem* **2019**, *6* (12), 2984-2997.
- [68] Lee, S.; Kwon, G.; Ku, K.; Yoon, K.; Jung, S. K.; Lim, H. D.; Kang, K., Recent progress in organic electrodes for Li and Na rechargeable batteries. *Adv. Mater.* **2018**, *30* (42), 1704682.

- [69] Lee, S.; Hong, J.; Kang, K., Redox-active organic compounds for future sustainable energy storage system. *Adv. Energy Mater.* **2020**, *10* (30), 2001445.
- [70] Mulzer, C. R.; Shen, L.; Bisbey, R. P.; McKone, J. R.; Zhang, N.; Abruña, H. c. D.; Dichtel, W. R., Superior charge storage and power density of a conducting polymer-modified covalent organic framework. *ACS Cent. Sci.* **2016**, *2* (9), 667-673.
- [71] Halder, A.; Ghosh, M.; Khayum M, A.; Bera, S.; Addicoat, M.; Sasmal, H. S.; Karak, S.; Kurungot, S.; Banerjee, R., Interlayer hydrogen-bonded covalent organic frameworks as high-performance supercapacitors. *J. Am. Chem. Soc.* **2018**, *140* (35), 10941-10945.
- [72] Yusran, Y.; Li, H.; Guan, X.; Li, D.; Tang, L.; Xue, M.; Zhuang, Z.; Yan, Y.; Valtchev, V.; Qiu, S., Exfoliated mesoporous 2D covalent organic frameworks for high-rate electrochemical double-layer capacitors. *Adv.Mater.* **2020**, *32* (8), 1907289.
- [73] Khayum, A.; Ghosh, M.; Vijayakumar, V.; Halder, A.; Nurhuda, M.; Kumar, S.; Addicoat, M.; Kurungot, S.; Banerjee, R., Zinc ion interactions in a two-dimensional covalent organic framework based aqueous zinc ion battery. *Chem. Sci.* **2019**, *10* (38), 8889-8894.
- [74] Wang, W.; Kale, V. S.; Cao, Z.; Kandambeth, S.; Zhang, W.; Ming, J.; Parvatkar, P. T.; Abou-Hamad, E.; Shekhah, O.; Cavallo, L.; Eddaoudi, M.; Alshareef, H. N., Phenanthroline covalent organic framework electrodes for high-performance zinc-ion supercapattery. *ACS Energy Lett.* **2020**, *5* (7), 2256-2264.
- [75] Yang, Y.; He, X.; Zhang, P.; Andaloussi, Y. H.; Zhang, H.; Jiang, Z.; Chen, Y.; Ma, S.; Cheng, P.; Zhang, Z., Combined intrinsic and extrinsic proton conduction in robust covalent organic frameworks for hydrogen fuel cell applications. *Angew.Chem.Int.Ed.* **2020**, *132* (9), 3707-3713.

Exceptional Capacitance Enhancement of a Non-Conducting COF through Potential-Driven Chemical Modulation by Redox Electrolyte



2.1. Introduction:

The insufficient capability of energy-storage devices often limits recent technological advancements in diverse fields, including portable electronics, transportation, and green energy.^[1–3] The unique features of supercapacitors, such as high power density, fast charging/discharging time, and high cycle stability, entice various applications.^[4,5] However, the energy density of the supercapacitors for these applications demands further improvement. Recently, the covalent organic framework (COF) has generated tremendous attention in the field of energy storage due to its unique structural and functional properties.^[6–8] The tunable porosity, ordered structures with atomic-level precision, and high accessible surface area make COFs as a promising candidate for supercapacitors.^[9–11] The long-range ordering of COF pores devises the unique ion channel, which assists the ultra-fast percolation of ions and creates an excellent interface between electrode and electrolyte. The high surface area of COFs contributes to the electric double-layer capacitance (EDLC) part, and the redox behavior of heteroatom(s) present in the framework imparts pseudo-capacitance. Previously, triazine and β -ketoenamine COF have been employed for good gravimetric capacitance in aqueous electrolytes.^[11,12] These COFs showed pseudo-capacitive behavior along with the EDLC, which could be well understood from their cyclic voltammograms (CVs) and galvanostatic charge–discharge (GCD) curves.^[13] The poor electrical conductivity of COFs limits the performance of supercapacitors. However, various strategies were employed to improve the conductivity to get a better capacitive performance of COFs.^[14–16] To enhance the conductivity of 2D COFs, Dichtel and co-worker introduced EDOT to DAAQ-TFP COF via facile electropolymerization within the pores, and COF films were achieved very first time. The PEDOT-modified DAAQ-TFP COF exhibited high capacitance (350 F/cm³). Later, Mai and co-workers synthesized a composite of polyaniline and COFs for supercapacitors (95 F/g at a current density of 0.2 A/g).^[17,18] There is one impediment to this approach. The polymer grown in the pores can block and ruin the inherent porosity of the COF. Hence, alternatively, a great enhancement of capacitance can be achieved by introducing redox electrolyte instead of the inert electrolyte.^[19,20] The improved performance in such a system is attributed to high-speed Faradaic reactions, which impart very high pseudo-capacitance. A variety of redox-active electrolytes have been employed, such as Cu²⁺ (1335 F/g at a current density of 60 A/g), iodine (685 F/g at a scan speed of 1 mV/s), bromine (572 F/g at 2 mA/cm²), hydroquinone (901 F/g at 2.65 mA/cm²), methylene blue for hybrid capacitors (279 F/g at 0.88 mA/cm²).^[21–26] Fischer and co-worker reported Potassium iodide KI as a redox additive on pyrolyzed MOF based

ultrathin hierarchical porous carbon nanosheets for exceptional high capacitance (1636 F/g at 5 mV/s).^[27] Later, Gomez-Romero and co-workers showed paper-based hybrid micro-supercapacitors with noticeable volumetric capacitance (130 mF/cm³ at 6.5 mA/cm³).^[28] This micro-supercapacitor is made by coating graphene on paper with a well-optimized geometry in terms of areal capacitance. And there, they find ~ 4.3 times enhancement in performance as they include KI into the H₂SO₄ electrolyte. In our case, we have more of a bulk-capacitor device not specifically optimized for areal capacitance (particle size, soaking kinetics, electrode pressing). Yet our COF-derived pseudocapacitor with KI gives a ~6.5 times enhancement in areal capacitance for the solid-state device. This could mean there is a lot of room for improvement. We realized these redox-active supporting electrolytes could gain an immense advantage when allowed to adsorb into the carbon-activated mesoporous sponge- the COF. A word of caution: In many reports, the capacitance is determined from three-electrode measurements,^[6,7,11,12,14-16,18-22,24,29] which may not be accurate. The reason being, a capacitance value relies on a potential difference between two electrodes and not the absolute position of one electrode only, which is measured in a three-electrode system against a reference electrode. The capacitance and derived values depend strongly on the potential of an arbitrary reference electrode and, therefore, may not translate to the device-level performance. Henceforth, it is more appropriate to report capacitance and energy density values extracted from two-electrode solid-state devices for practical comparisons (see additional remarks in SI).^[9,10,13,17,23,25,26,28,30]

Here we have used both three- and two-electrode studies to reveal synergistic coupling of an electronically non-conducting COF (conductivity = 3.16×10^{-4} S/cm) with an electrolyte containing KI as the redox-active additive. The outcome is an exceptional enhancement in pseudo activity along with EDLC of the capacitance. This KI as an additive, under a redox potential, generates a variety of active species, most of which reversibly adsorb on the COF sponge. The role of carbon (15%), as an electronic activator, in boosting the redox activity at the COF-derived electrode is also precisely established through suitable controls. Our detailed analysis coupling insitu UV-vis and operando Raman spectro-electrochemistry with support from XPS consolidate the presence of iodine/iodide/iodate type intermediates. Inspection reveals the predominance of I₃⁻ species on the COF surface giving rise to an associated redox activity registered by the CV. The favorable interactions of I₃⁻ within the pore environment of the COF under an external electric field are endorsed through DFT studies. As a practical solid-state device, it displays a specific capacitance of 56.37 ± 7.57 F/g yielding the best energy density of 4.96 ± 0.67 Wh/kg with a power density of 51.59 ± 4.01 W/kg. The prominent

capacitance enhancement of a non-conductive COF by a dynamically generated mild but highly polarizable redox species ushers numerous possibilities.

2.2. Results:

2.2.1. Synthesis and Characterizations of the Triazine-Phenol COF (IISERP-COF25):

2,4,6-triformylphenol (55 mg, 0.3 mmol) and 2,4,6-Tris(4-aminophenyl)-s-triazine (107 mg, 0.3 mmol) were weighed into a Pyrex liner and was dissolved in ortho-dichlorobenzene (3.0 mL) and mesitylene (3.0 mL) and ethanol (3 mL) stirred for 30 mins (Scheme 1). To this mixture, 1.0 mL of 6M acetic acid was added. Then it was flash-frozen in a liquid nitrogen bath and sealed. Contents were heated in an oven at 120° C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded about 120 mg of dark red-colored solid (Figure 2.1.), which was washed with hot DMF, dioxane, MeOH, acetone, and THF (85%, isolated yield). The product was also subjected to Soxhlet extraction using DMF/methanol as solvents. The final product was characterized by NMR analysis and IR.

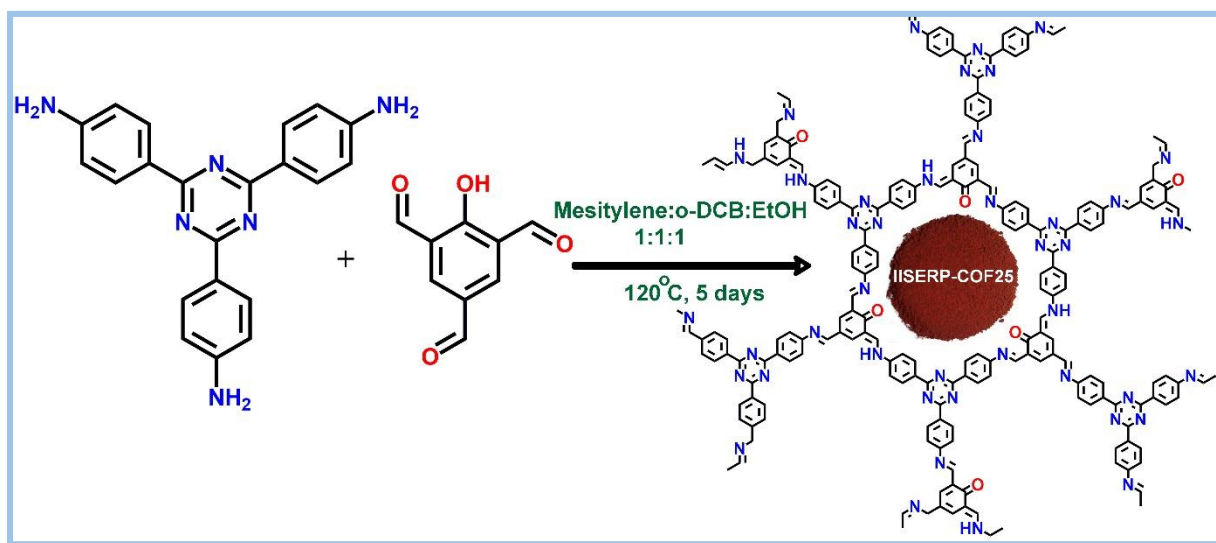


Figure 2.1. The synthesis of IISERP-COF25.

The presence of suitable peaks corresponding to the triazine group, Schiff bonds ($-C=N-$), and absence of any terminal amine or aldehyde groups in the solid-state NMR and infrared (IR) spectra of the COF implies a high degree of completeness of the polycondensation reaction. It also surmises that the monomers retain their functional group integrity during the polymerization (Figures 2.2. and 2.3. and Table A.2.1.).

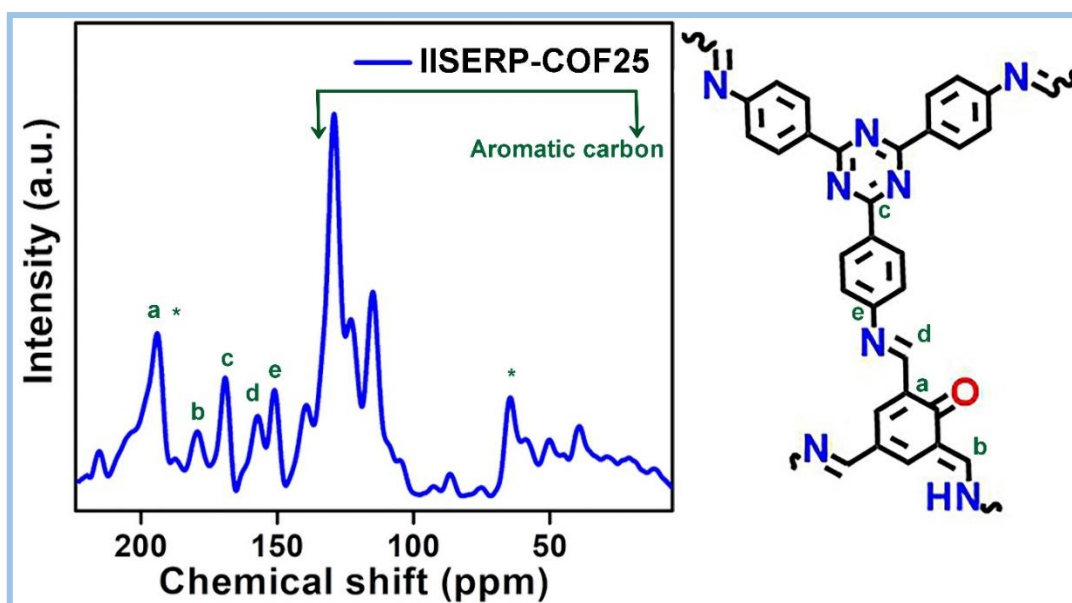


Figure 2.2. CP MAS ^{13}C -NMR spectra of the COF at 500 MHz. a,b,c,d,e are the positions of the corresponding peaks obtained from the NMR data. * - Corresponds to the sidebands. The synthesis of IISERP-COF25. The majority of the COF exists in the β -ketoenamine with highly stabilized imine bonds

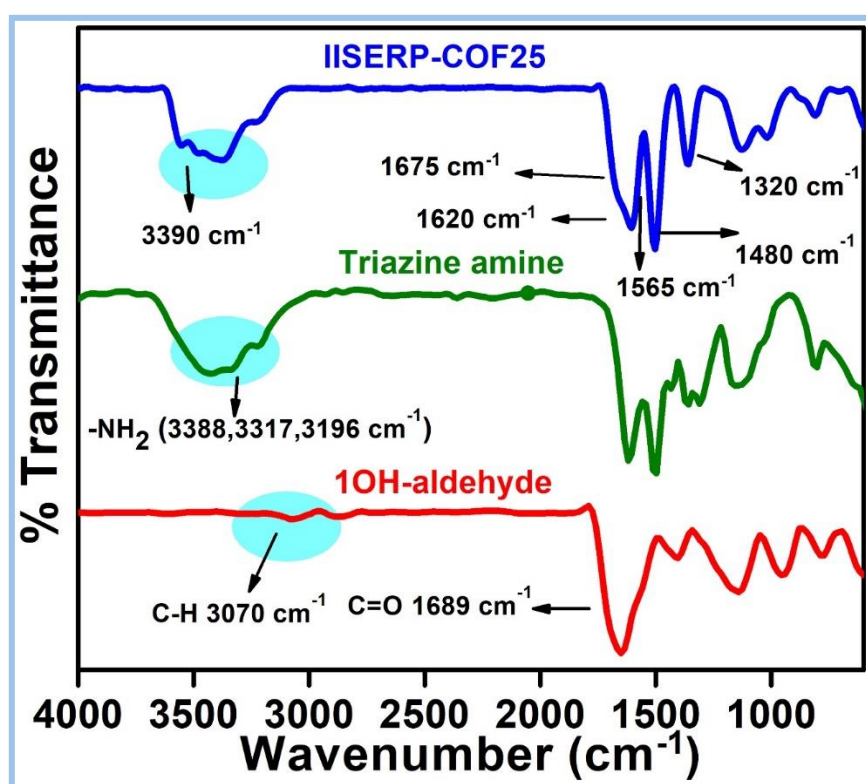


Figure 2.3. CP MAS ^{13}C -NMR spectra of the COF at 500 MHz. a,b,c,d,e are the positions of the corresponding peaks obtained from the NMR data. * - Corresponds to the sidebands.

2.2.2. Structure modeling of IISERP-COF25:

The porous structure was solved from atomic modeling carried out using Materials Studio. Both eclipsed and staggered models were considered, and the former fits much better with the experimental Powder XRD (Figures 2.4. and A.2.1., Appendix). A structure was modeled in P1 and geometry optimized using the CASTEP routine (Figure 2.4.). The final structure was refined through Pawley methods (P1, $a = 18.6396(5)\text{\AA}$; $b = 18.6415(5)\text{\AA}$; $c = 3.5306(2)\text{\AA}$; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 120.034^\circ$, Figure 2.4.). The 3+3 monomer combination could have adapted to the P6/m space group, however, the presence of the phenolic –OH moiety in the trialdehyde monomer makes it asymmetric and lowers the overall symmetry of the refined structure to triclinic, P1 (Table A.2.2.).

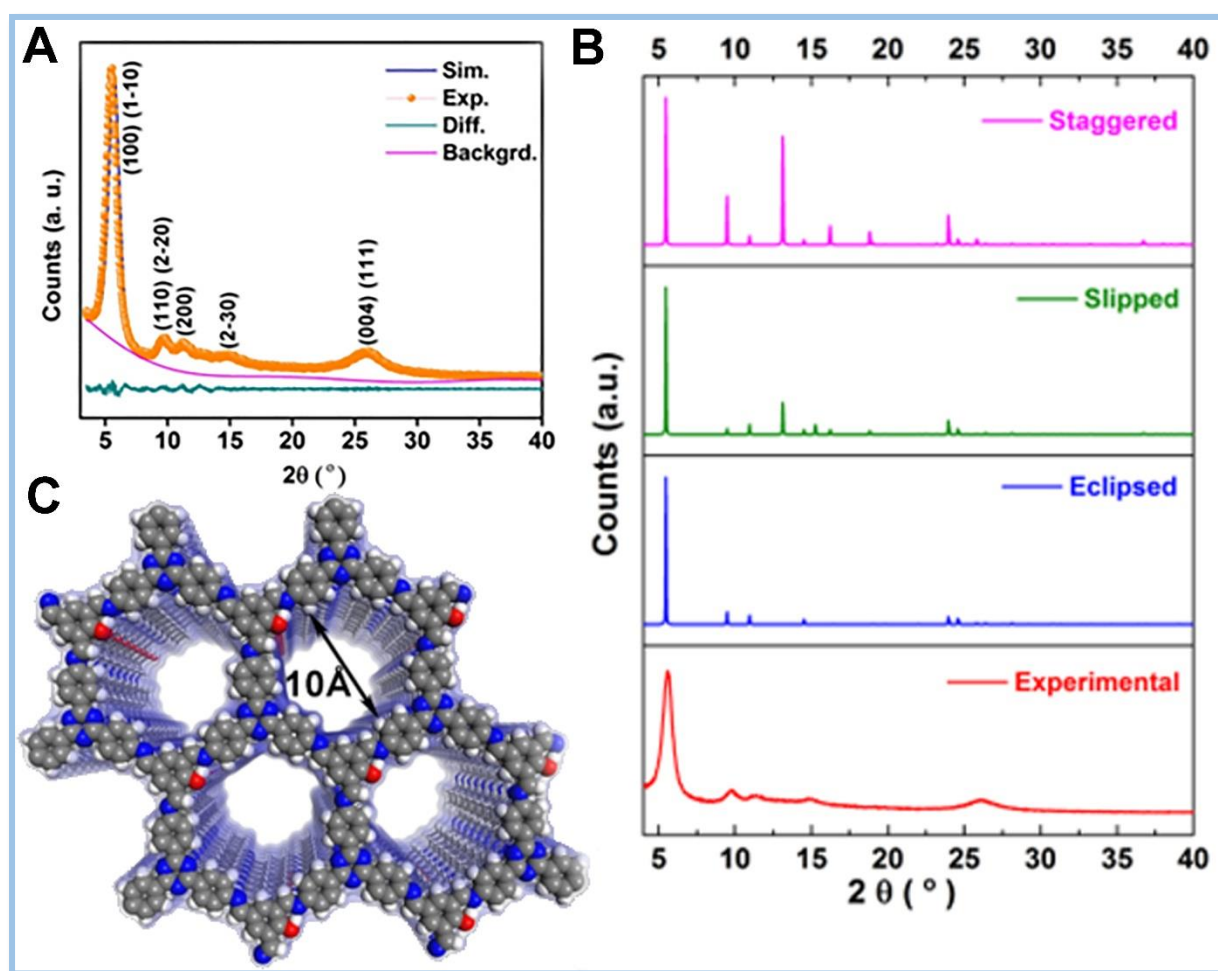


Figure 2.4. (A) A Pawley refinement of the eclipsed model against the experimental PXRD pattern. (B) A comparison of the simulated PXRD pattern of the structure with different layer arrangements with the experimental PXRD pattern. (C) 3D DFT-optimized structure of IISERP-COF25.

The refined 3D structure showed uniform 1-D channels (~ 10 Å) lined by proximally positioned keto/phenol, pyridyl (triazine), and Schiff groups. The results from the bulk characterizations agreed well with this AAA... stacked honeycomb model (Figures 2.4. and A.2.2., Appendix).

2.2.3. Characterization: Porosity and morphology

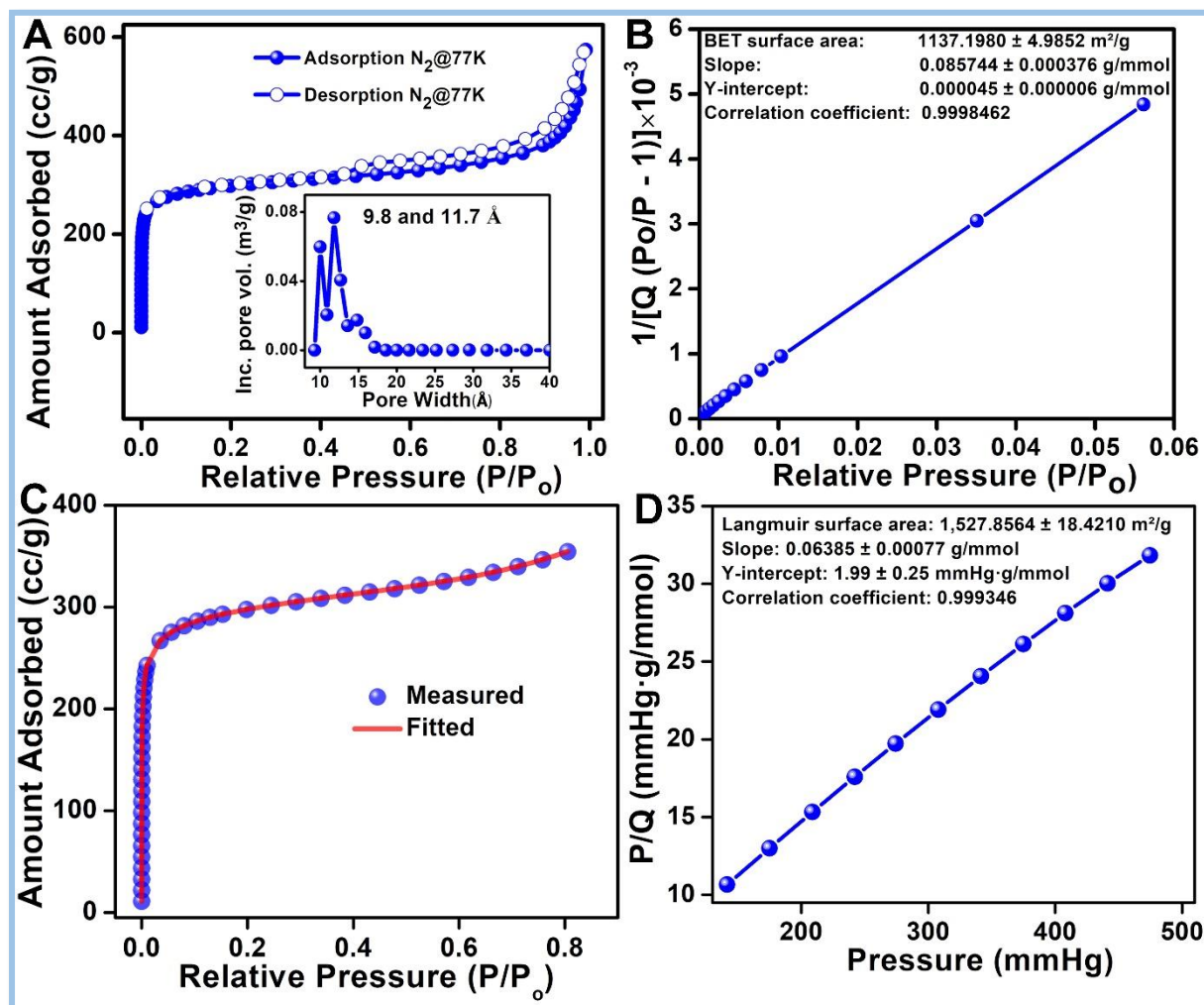


Figure 2.5. (A) N₂ adsorption-desorption isotherms of IISERP-COF25 at 77 K. Inset show a plot of the pore width vs. incremental pore volume of the COF. (B) A BET fit obtained using the low-pressure region data of the N₂ adsorption isotherm. (C) The goodness-of-fit plot of the adsorption isotherm from the DFT model (Carbon at 77K). (D) A Langmuir fit obtained using the N₂ adsorption isotherm.

The as-synthesized COF yielded a completely reversible type-I nitrogen adsorption isotherm characteristic of a microporous structure (Figure 2.5.A, pore sizes 9.8 and 11.7 Å), with a Brauner-Emmet-Teller (BET) surface area of 1137 m²/g and Langmuir surface area of 1527 m²/g obtained (Figure 2.5.), A which is lower than the surface area estimated from a perfectly

eclipsed model. COF soaked in HCl (3M), H₂SO₄ (3M), and NaOH (3M) shows exceptional chemical stability, retention of porosity, and functional group integrity (Figure 2.6.A). Thermogravimetric analysis (TGA) and variable temperature PXRDs show the thermal stability of the COF (stable up to ~ 300 °C) (Figures 2.6.A, and A.2.3.). Under HRTEM, the fibers can be seen to have formed from few-layer thick stacked plates. HRTEM shows fine micron-sized pores all along the surface. These are crucial for both electrolyte diffusion and close interactions between the framework and the charged-guest species.^[30,33-34] Also, significant crystallinity was deciphered from well-defined lattice fringes and SAED, which could be indexed to the COF-interlayer d-spacings and few other low-angle reflections expected from the modeled structure (Figures 2.7.-2.10. and A.2.4.-A.2.7.).

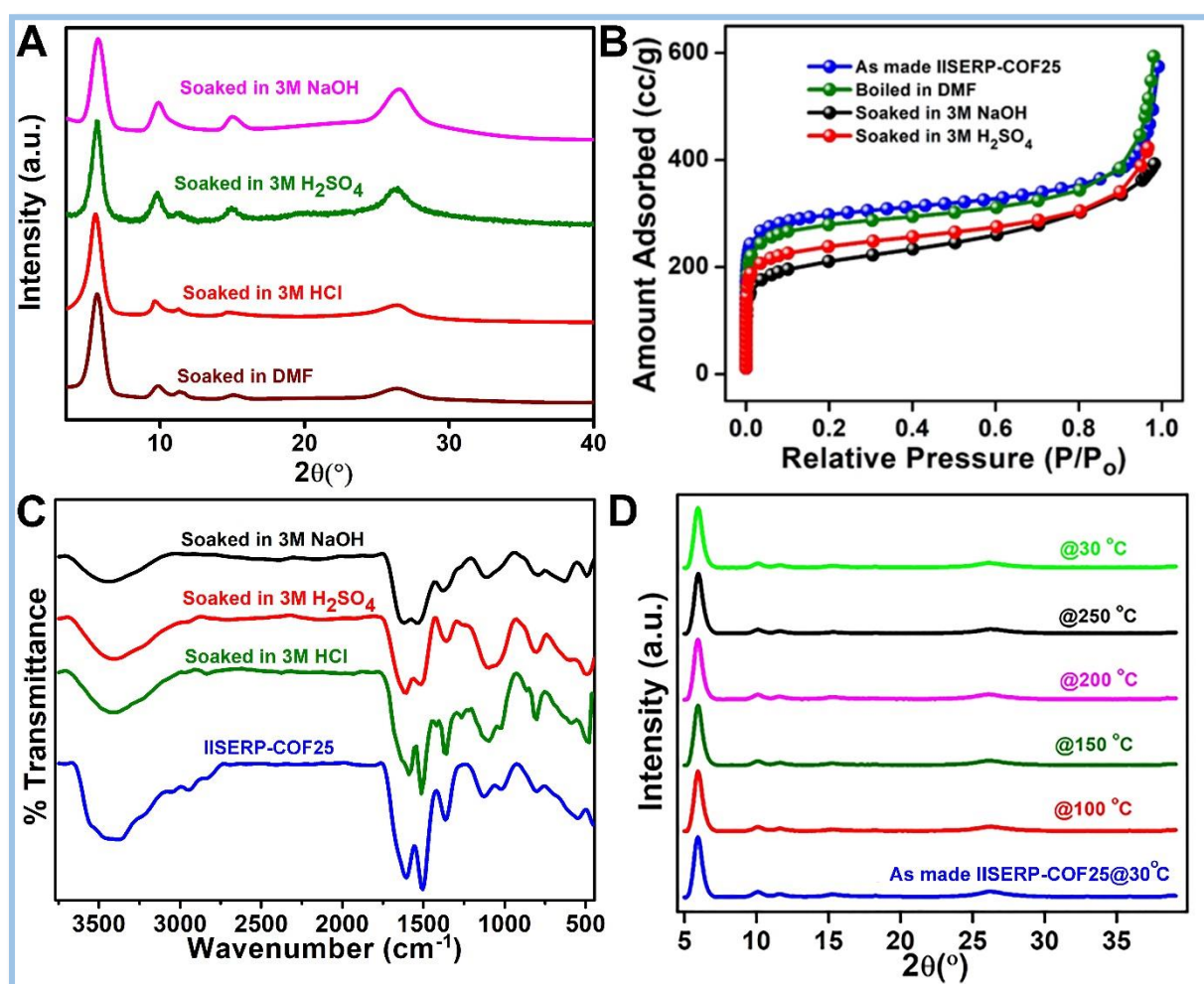


Figure 2.6. (A) PXRD patterns of the COF soaked in acids, bases, and solvents displaying the COF's chemical stability. (B) N₂ 77K adsorption of the COF after boiling in DMF, after acid and base treatment. (C) IR patterns of the COF that were soaked in acids and bases. (D) Variable temperature PXRDs of the neat COF.

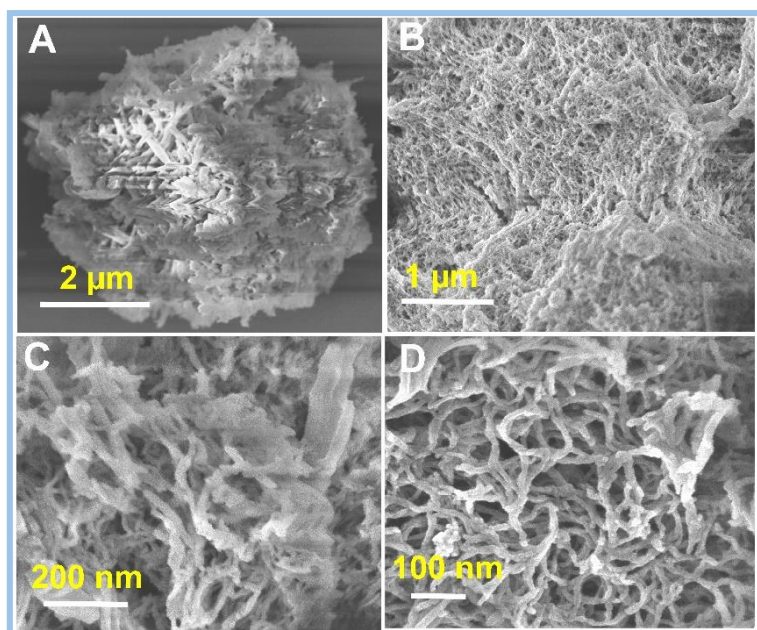


Figure 2.7. (A) FESEM images of IISERP-COF25 at different resolutions. It shows flaky hexagonal morphology. At the lower resolution, a fluffy cotton-like morphology can be seen. Whereas at higher resolution, the presence of tubular or fibrous morphology can be seen.

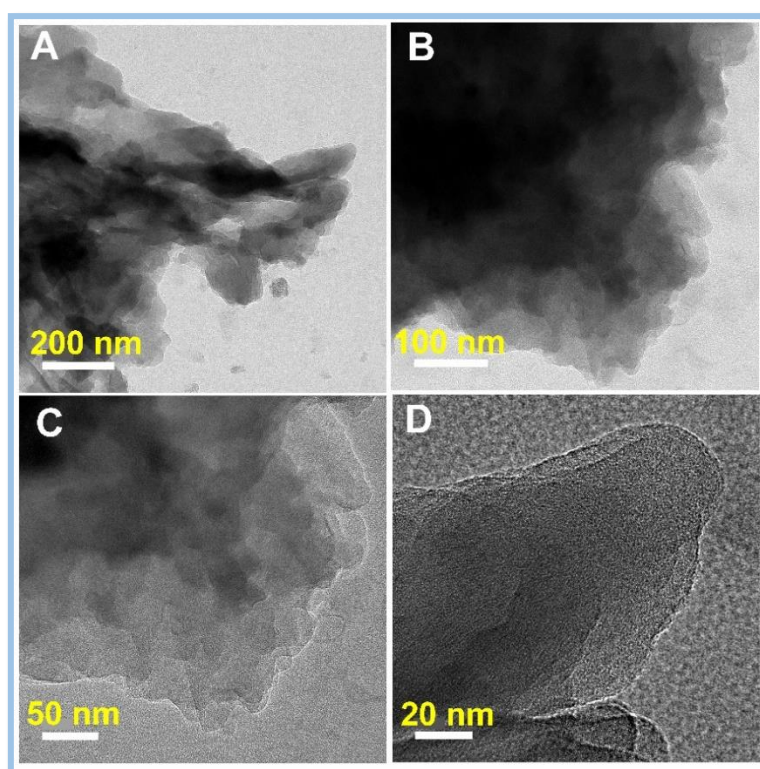


Figure 2.8. (A) HRTEM images of the IISERP-COF25 under different magnifications showing the aggregates formed by the stacking of many hexagonal sheets.

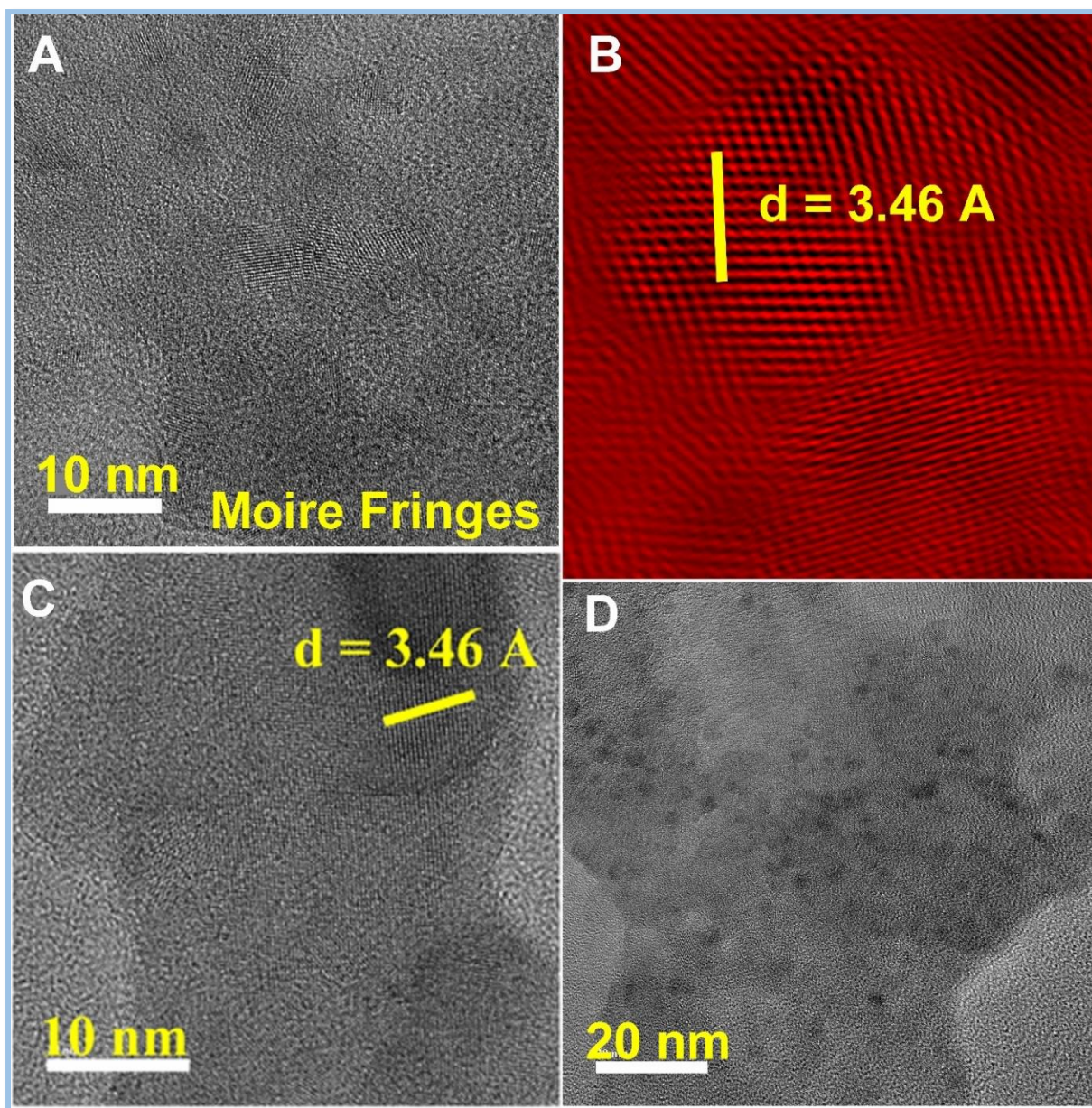


Figure 2.9. (A) HRTEM images of the as-synthesized IISERP-COF25 showing several overlapping crystalline flakes giving rise to Moire Fringes. (B) and (C) At higher resolution, the stacked layers giving rise to lattice fringes with d-spacing corresponding to the interlayer spacing of 3.46 Å can be seen. (D) At a lower resolution, many tiny COF flakes showing lattice fringes can be seen.

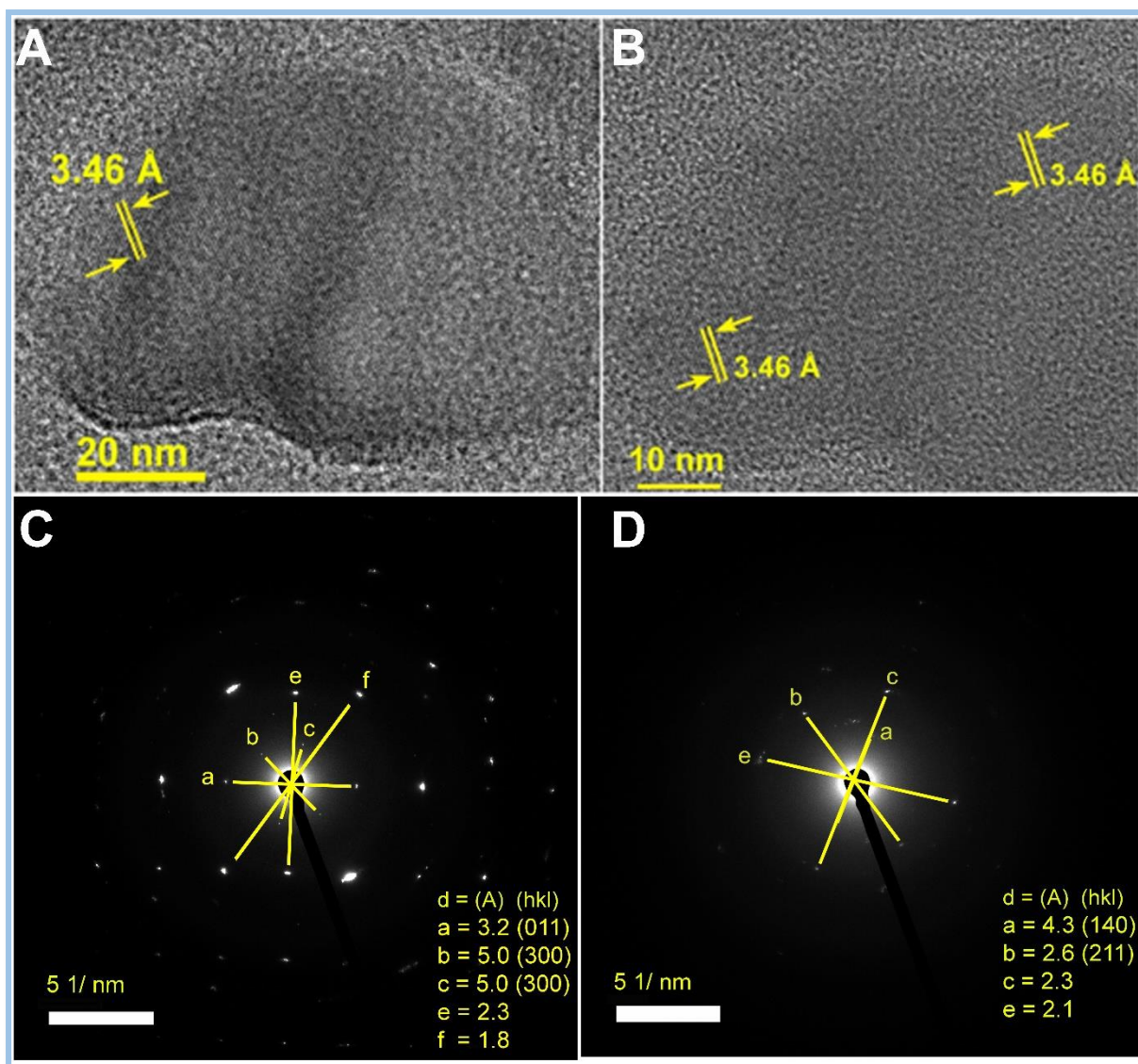


Figure 2.10. (A, B) HRTEM images from different flakes of the as-synthesized IISERP-COF25 show overlapping lattice fringes. Many regions show a separation of 3.46 Å, which correspond to the interlayer spacings (model: 3.53 Å). Note the above images show lattice fringes of the same d-spacing suggesting them to be highly crystalline single flakes. (C,D) The SAED pattern of the as-synthesized IISERP-COF25 shows the diffraction spots from different planes, some of them could be indexed to the hkl planes expected from the modeled structure. Some of them correspond to the higher-order reflections. Note: Similar type of SAED and lattice fringes are reported in COF literature (*Kuehl et al J. Am. Chem. Soc.* **2018**, *140*, 51, 18200–18207. *Shi et al Nat Commun* **2020**, *11*, 178., *Haase et al Mater. Chem. Front.*, **2017**, *1*, 1354-1361).

Note: Some of the reflections in the SAED, particularly lying far away from the central beam could not be indexed. They could be coming from some other COF flake which is differently oriented with respect to the flake whose reflections have been indexed.

2.2.4. Capacitor and Impedance Measurements in a Three-Electrode Set-Up

To secure an initial assessment of the electrochemical activity of the COF-carbon composite, a standard three-electrode system with 1M H₂SO₄ as the electrolyte, composite coated Toray carbon paper of 1 cm x 1cm as the working electrode, Ag/AgCl as the reference, and large platinum as the counter electrode with a geometrical area bigger than the working electrode. Note that we have preferred a very thin uniform coating of the composite on the larger geometrical surface of a Toray paper (1 cm × 1 cm, ≈2 mg) over a typical glassy carbon, as this minimizes the errors in charge-storage quantifications (For comparison, the data collected using traditional glassy carbon electrode is presented in the Appendix). The working electrode was prepared by mixing 80% COFs, 15% Super P carbon, and 5% of Nafion binder in an ethanolic solution. The slurry was coated on the Toray carbon electrode. The working potential window of the COF was established from CV measurements (Figure 2.11.A). Three distinct redox peaks were observed, which manifest a redox behavior in addition to the surface charge storage. These redox peaks are attributed to the presence of functional groups such as triazine, phenyl, Schiff-base nitrogens, and enolizable keto groups in the COF (Figure A.2.8.).^[30, 35] The composite electrode stores about $1469 \pm 128 \text{ C g}^{-1}$ in this redox electrolyte, GCD curves, whereas the electrode coated with the same loading of only neat Super P carbon displays a capacitance of $278 \pm 23 \text{ C g}^{-1}$ (Figures A.2.9-A.2.12, and Equation A.2.1).^[30] Realizing that this COF-carbon composite requires substantial capacitance enhancement in charge storage to qualify for practical usage, we resorted to a redox electrolyte system.^[20-28] Here, we adopted a distinct strategy involving the use of “redox electrolyte.” We choose KI as a redox additive, owing to its exceptionally low toxicity, environmentally benign nature, and mainly for its ability to form a spectrum of redox-active species. Under the redox potential, KI can generate stable polyiodide ions (I_n)⁻ with different redox pairs of iodide on the surface of the electrode, such as $3I^-/I_3^-$, $2I^-/I_2$, $2I_3^-/3I_2$, and $I_2/2IO_3^-$.^[22, 23, 27] The facile movement and percolation of such species can benefit from a porous charge-storage system. The I^-/I_3^- redox couples have been studied earlier as redox additive in the electrolyte.^[27, 28] However, most of the reports are based on activated carbon electrodes and carbon-derived from MOF pyrolysis.^[27] All such carbons generally carry high conductivity, which makes them a far-away antecedence for the typically non-conducting COF and polymers. Here, we report for the first time the use of a redox-active additive (KI) enriched H₂SO₄ as the electrolyte for COF-based charge-storage.

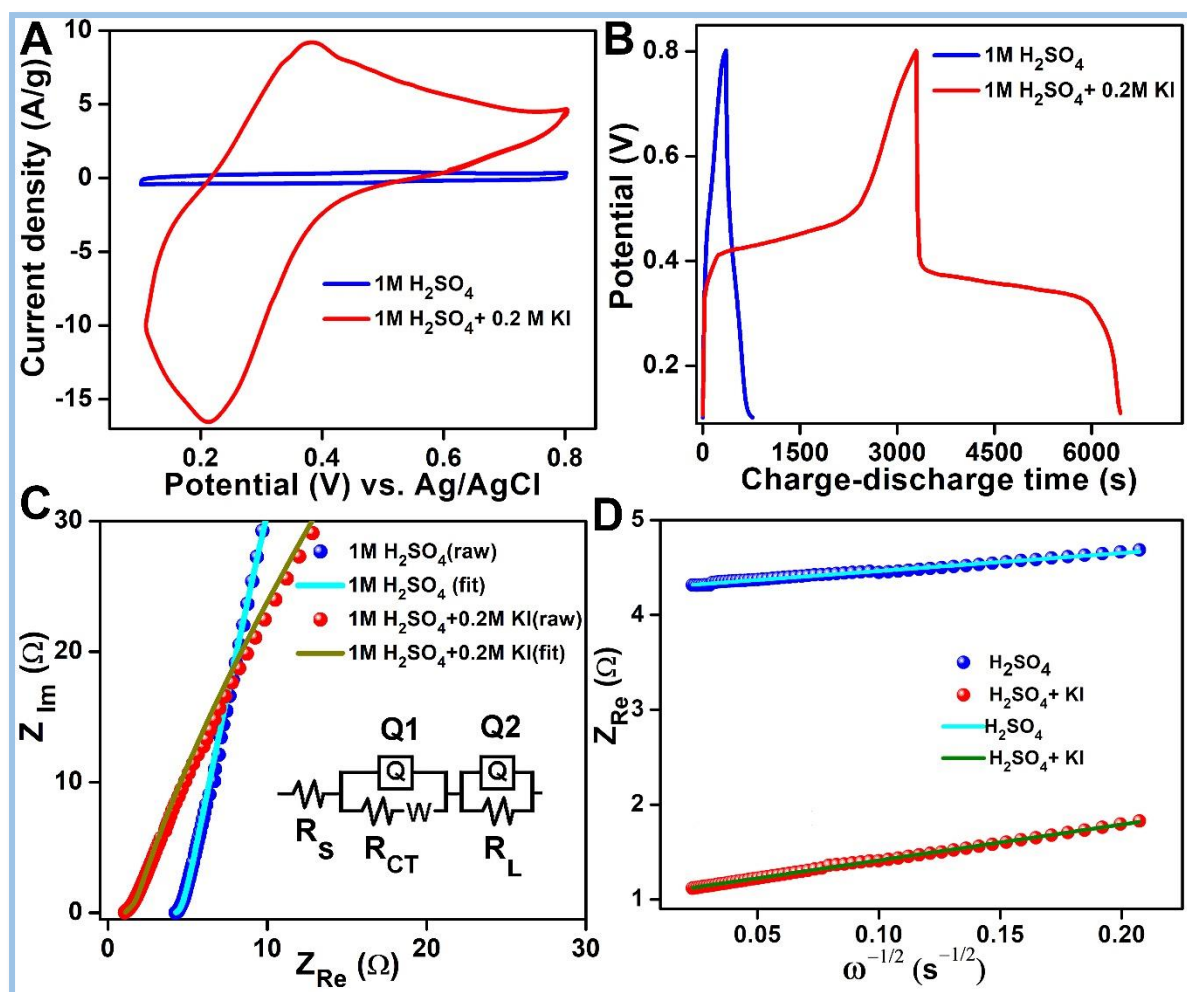


Figure 2.11. (A) Comparative CV plots of the composite-electrode measured using 1M H₂SO₄ and 1 m H₂SO₄ + 0.2 M KI as electrolyte in a three-electrode assembly @2 mV s⁻¹ scan rate with a 2 mg loading of the composite, Toray carbon paper as working electrode. B) Comparative Galvanostatic charge–discharge profile of the composite within the potential window of 0.1–0.8 V @500 mA g⁻¹ current density, measured in the three-electrode assembly. C) Nyquist plots from the AC-impedance measurements of the composite using the three-electrode assembly. D) A plot of the Z_{Re} versus ω^{-1/2} of composite measured using the three-electrode assembly. Note: In (C) and (D), circle = experimental data; Line = calculated fit.

Discernible changes occur in their CV curves: The KI + H₂SO₄ system covers an extra-large area compare to neat H₂SO₄ (Figure 2.11.A). A substantial enhancement in the overall current was observed from the CV and superior charge discharge were observed from the galvanostatic charge–discharge measurements (Figure 2.11.B). Thus, KI in H₂SO₄ can form iodine/iodide at the electrode/electrolyte interface under a potential.^[28] However, the coulombs per gram estimated using these three-electrode measurements (half-cell) are not a proper evaluation of

the material's performance as a capacitor, but it indicates the electrochemical enhancement brought about by combining the COF-derived electrode with the redox electrolyte. Later we have described a more accurate quantification of the capacitance via two-electrode measurements.

To decipher the mechanism of charge storage in the composite electrode from the CV, a plot of the log of anodic peak current versus log of scan rate yields a value of 0.81 for neat H_2SO_4 , which suggests more of a surface-controlled behavior, in contrast, when the KI is present in the electrolyte, this has a value of 0.66, which indicates more of a redox-activity (Figure A.2.13.). Electrochemical impedance spectroscopy was used to compare the ion-transport behavior and electrode–electrolyte resistance using a three-electrode assembly (Figure 2.11.C). Both the H^+ and the polyiodide interactions with the composite-coated electrode was modeled using the modified linear equivalent circuit suggested for porous materials (Figure A.2.17).^[25-28, 36-40] Constant phase elements (CPE) were used in the equivalent circuit model instead of simple capacitors, considering the pseudocapacitive nature of our system.^[41-44] The R_s represent the contribution from the ionic resistance of the electrolyte and the intrinsic electronic resistance of the electrode material. R_{CT} placed parallel to the CPE (Q_1) represents the charge transfer resistance, which characterizes the rate of redox reactions at the electrode–electrolyte interface. R_L is the leakage resistance placed parallel to the constant phase element (Q_2), which accounts for the mass capacitance in the low-frequency regime. The same equivalent circuit was employed for fitting all the Nyquist curves, using the ZsimWin software. The fits yielded low χ^2 values and >2.5% error. The observed resistance R_s , R_{CT} , and R_L , are all in the acceptable range.^[41, 44, 45] The Nyquist plot of the COF shows a diffusion-limited electrochemical process comparable to many conductive and non-conductive polymers^[45] and a redox-active pseudocapacitor, RuO_2 in Graphene.^[41, 46-49] In our three-electrode set-up, between the composite electrode in H_2SO_4 and the $\text{KI} + \text{H}_2\text{SO}_4$, considering that the only major variable is the electrolyte resistance, we find that the R_s decreases substantially upon adding the KI ($4.5 \, \Omega$ for H_2SO_4 versus $1.1 \, \Omega$ for $\text{KI} + \text{H}_2\text{SO}_4$) (Figure 2.11.C). The R_{CT} values for both H^+ and the polyiodide were very small, as is seen from the Nyquist plot ($R_{CT}(\text{H}^+) = 0.8$; $R_{CT}(\text{polyiodide}) = 0.2$), comparable to other redox electrolyte systems.^[44, 50] A well-defined Warburg tail was observed for both electrolyte systems. The projected length of the Warburg curve on the real impedance axis (ZR_e) characterizes the ion penetration process,^[51] and this Warburg component was larger for the redox electrolyte, suggesting that the diffusion of the polyiodide species into the electrode was slower and more resistive compared to the protons.

This is expected, given the larger size of the polyiodide, further confirmed by a plot of the ZR_e versus $\omega^{-1/2}$. The resulting linear fit yields a slope (Warburg constant) of $3.8 \text{ s}^{-1/2}$ for the composite in the redox electrolyte and $1.9 \text{ s}^{-1/2}$ in neat acid (Figure 2.11.D). Thus the polyiodide has approximately two times higher Warburg component than the H^+ . “n” values for both the constant phase elements indicate the pseudocapacitive nature (Table A.2.4.). The leakage resistance placed parallel to the Q_2 seems to be high and can be neglected.^[41] The impedance measurements were done using neat COF-coated electrodes to get further insights into the interaction of the redox electrolyte with the COF (Figures A.2.18. and A.2.19.). Fortified, we evaluated the capacitance of the COF-derived solid-state capacitor by employing more practical two-electrode measurements.

2.2.5. Measurements on a Flexible Solid-State Capacitor Device in a Two-Electrode Configuration

The solid-state capacitor was fabricated by coating slurry made using 80% the COF dispersion in ethanol, 15% of Super P carbon, and 5% of polyvinylidene fluoride (PVDF) binder on a 1 cm^2 carbon cloth and Celgard as a separator. Variable scan rate (2.5 to 500 mV s^{-1}) CV measurements were conducted in the range of 0 – 0.8 V using these solid-state capacitors using polyvinyl alcohol (PVA)- H_2SO_4 and PVA- $\text{H}_2\text{SO}_4 + \text{KI}$ gel electrolyte. An archetypal rectangular-shaped CVs is observed at low (Figure 2.12.A) and high scan rates (Figure A.2.23.) in the PVA- H_2SO_4 gel electrolyte case.^[52] Their areal capacitances calculated from the GCD (using Equation A.2.3, Figures 2.12.B; Figures A.2.21. and A.2.24.) delivers a specific capacitance of $41 \pm 4 \text{ mF cm}^{-2}$ at 0.5 mA cm^{-2} for PVA H_2SO_4 gel electrolyte and $270 \pm 11 \text{ mF cm}^{-2}$ for PVA- $\text{H}_2\text{SO}_4 + \text{KI}$ gel electrolyte. The observed value is among the best-performing MOF/COF-derived solid-state capacitors reported so far (Table A.2.11.). This capacitance enhancement approves the charge/area enhancement evidenced by the three-electrode measurements. This high solid-state areal capacitance is sustained over a wide range of current densities (from 0.5 to 5 mA cm^{-2}) with an acceptable drop in capacitance (Figures A.2.21., A.2.22., A.2.24., and A.2.25.). This reflects in the impressive power ($175 \pm 3 \mu\text{W cm}^{-2}$ at 0.5 mA cm^{-2}) and energy densities ($24 \pm 1 \mu\text{Wh cm}^{-2}$) (Tables 2.1., 2.2. and A.2.6.). Notably, the Coulombic Efficiency (CE) for composite in the redox electrolyte $78 \pm 3\%$. Typically, pseudocapacitance never has the same CE as EDLC owing to some irreversible binding.

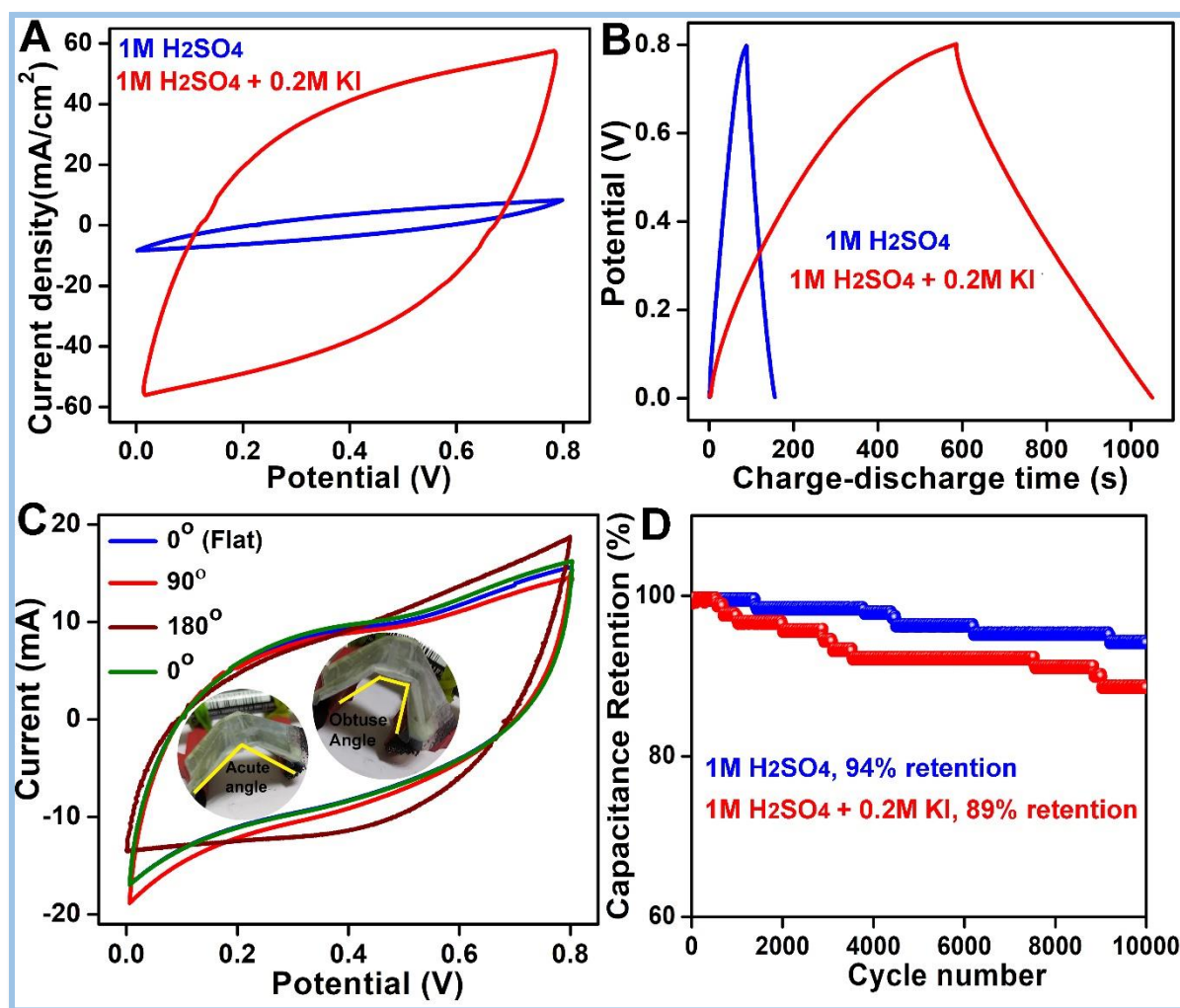


Figure 2.12. (A) Comparative CV plots of the COF-derived solid-state device (geometrical surface area = 1 cm^2) measured using $1\text{M H}_2\text{SO}_4$ and $1\text{M H}_2\text{SO}_4 + 0.2\text{M KI}$ as electrolyte @ 500 mV s^{-1} scan rate with a 10 mg total loading. (B) Comparative Galvanostatic charge–discharge curves from the solid-state device measured using $1\text{M H}_2\text{SO}_4$ and $1\text{M H}_2\text{SO}_4 + 0.2\text{M KI}$ as electrolyte. (C) CV curves at different mechanical states by bending at different angles. The angles are approximate. (D) Cyclic stability of the composite containing solid-state device measured over 10 000 cycles.

Additionally, some charge leakage and diffusion limitation for the large-sized polyiodides can also contribute to this. The device fabricated using $\text{H}_2\text{SO}_4 + \text{KI}$ gel electrolyte was tested for different mechanical states by bending at different angles (obtuse and acute) (Figure 2.12.C). CVs explicated the good mechanical stability exhibited by the solid-state device. The device fabricated using the PVA- H_2SO_4 gel retained 94% of its capacity after 10 000 cycles, while the one made using PVA- $\text{H}_2\text{SO}_4 + \text{KI}$ retained 89% of its capacity (Figure 2.12.D). When the same solid-state device was repressed mechanically and put back, it again starts with almost 100% capacitance.

Table 2.1. Comparison of the areal capacitance of the COF and MOF derived two-electrode symmetric solid-state devices.

Electrode material	Electrolytes	Working Voltage (V)	Current density (mA/cm ²)	Specific capacitance (mF/cm ²)	Ref.
CT-Dq1-Da1-Tp	PVA-H ₂ SO ₄ gel	0 to 1	0.39	8.5	35 ^c
CT-Dq-Tp	PVA-H ₂ SO ₄ gel	0 to 1	0.39	12	35 ^c
TpOMe-DAQ	PVA-2 MH ₂ SO ₄ gel	0 to 1	0.25	84	9 ^c
PANI-ZIF-67-CC	PVA-H ₂ SO ₄ gel	0 to 1	0.05	35	79 ^c
PEDOT-GO/UC	PVA-H ₂ SO ₄ gel	0 to 1	10 mV /s	102	62 ^c
IISERP-COF10	PVA-H ₂ SO ₄ gel	0 to 0.8	0.5	92	30 ^c
4h-Cu-CAT-NWAs	PVA-LiCl gel	0 to 0.8	1.25	252.1	77 ^c
IISERP-COF25	PVA-H ₂ SO ₄ gel PVA-KI+H ₂ SO ₄ gel	0 to 0.8	0.5	41.33 ±3.85 269.60 ±11.39	This work

Thus, most likely, the drop in capacitance over 10 000 cycles is due to gradual delamination of the active material (COF + carbon) from the current collector (the carbon cloth) due to repetitive charge–discharge operation or partial degradation of the COF material and also due to some irreversible reactions at the composite.

Table 2.3. Performance of the IISERP-COF25 compared with other redox-active electrolytes.

Electrode material	Electrolyte	reference electrode	Current density (A/g)	Specific capacitance (F/g)	Ref.
MWCNTs/Zr O ₂ //MWCNTs/WO ₃	Li ₂ SO ₄ + KI	Ag/AgCl	10 mV/S	720	<i>Sci. Rep.</i> 2016 , <i>6</i> , 25793. ^c
Activated carbon (commercial)	KOH +m phenylenediamine	Ag/AgCl	1	605.22	<i>J. Mater. Chem.</i> 2012 , <i>22</i> , 19025. ^a
NPS-800	H ₂ SO ₄ + KI	Ag/AgCl	1.2 5 mV/S	917 1636	<i>Adv. Mater.</i> 2018 , <i>30</i> , 1705789 ^c
IISERP-COF25	1 M H ₂ SO ₄ + 0.2 M KI	Ag/AgCl	0.5	2,098.59 ±182.68	This work

Type of measurement set-up used in these studies: a = three-electrode set-up only, b = two-electrode device only and c = both (two and three-electrode set-up)

2.2.6. Operando Spectro-Electrochemical Investigations of the In Situ Redox Species

In the presence of this reactive electrolyte ($\text{KI} + \text{H}_2\text{SO}_4$), the appearance of a prominent oxidation–reduction peak in the CV denotes the ongoing pseudo activity of COF with polyiodide species under the applied potential. In situ spectro-electrochemical data, operando Raman shifts, and the XPS of fully charged (iodized) electrode were recorded to investigate the redox phenomena and generation of active redox intermediate during the charging process.

2.2.6.1. UV–Vis Spectroscopy under Applied Potential

To carry out the Spectro-electrochemical measurements inside the UV cuvette a typical three-electrode setup was built (WE: COF coated on ITO plate, RE. Ag/Ag^+ aqueous, CE. Platinum net, $\text{H}_2\text{SO}_4 + \text{KI}$ electrolyte) and connected to the ocean optics instrument to observe the in situ changes of the UV–visible spectra (Figure A.2.28.). Then a chronoamperometry measurement was carried out (at 0.8 V) over 2 h with the help of the CH-charge discharge analyzer and at every 15 min interval, the UV–visible spectrum was recorded. In the absence of any applied potential, the first absorption maxima of the COF at a lower wavelength region (at 272 nm) arises from the phenyl and triazine backbone of the COF (Figure 2.13. A(i)). And a second (at 359 nm) and third (at 405 nm) absorption maxima appear from the keto and enol tautomeric species generated by the phenolic moiety (Figures 2.13. A(i,ii)).^[53-55] When a potential of 0.8 V is applied, a gradual decrease of the first peak's intensity and a simultaneous increase of the third peak's intensity was observed (Figure 2.13.A(iii)). Also, a noticeable red-shift of the whole spectrum occurs, which is due to the interaction of the electrolyte species with the COF under this potential. These changes bring out a high possibility of C-I interaction. The weakening of the relatively stronger $\text{C}=\text{C}$ (lower wavelength) and $\text{C}=\text{N}$ backbone of the COF and formation of the $\text{C}-\text{I}$ bond (higher wavelength) indicates the generation of some polyiodide species (such as I_3^- , I_5^-) from the electrolyte under potential. Such species can interact with the electron-deficient $\text{C}=\text{C}$ and $\text{C}=\text{N}$ backbone of the triazine units of the COF (Figures A.2.29. and A.2.29.; Table A.2.7.).

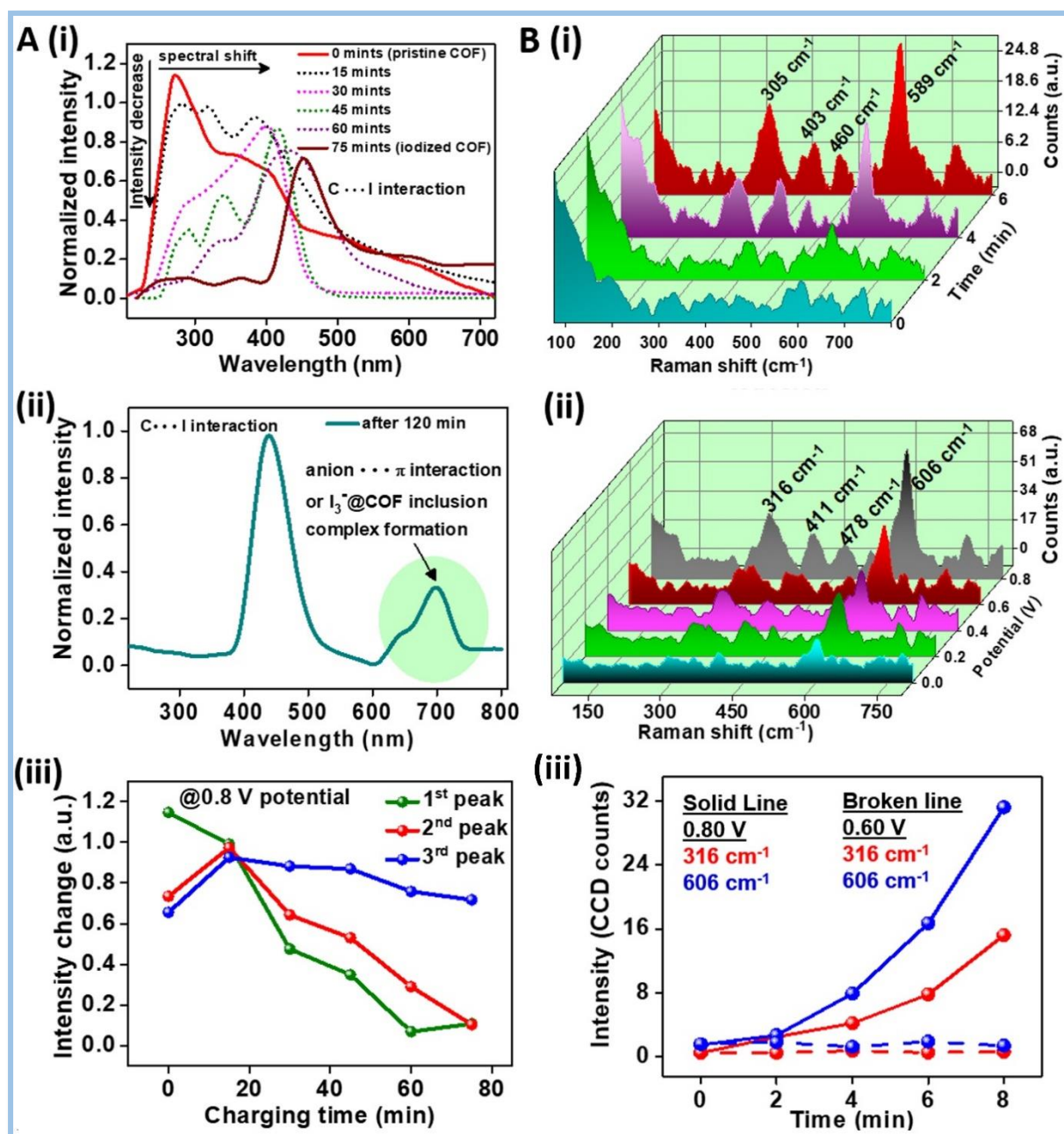


Figure 2.13. (A) (i, ii) In situ spectro–electrochemical data to monitor the change of UV–visible spectra of the IISERP-COF25 during chronoamperometry measurements. (iii) Intensity variation of absorption maxima of the COF with the progress of the chronoamperometry. B) (i, ii) Operando Raman spectra of the COF during chronoamperometry and chronopotentiometry measurements. B) (iii) Intensity variation of Raman-shift of the COF with the progress of the chronopotentiometry.

After a prolonged charging at 0.8 V, the peak centered around 698 nm arises because of the formation of some stable anion- π complex, most likely I_3^- @COF, an inclusion complex (Figure 2.13.A(ii) and Table A.2.7.). The formation of this charge-transfer complex is linearly correlated with the concentration of the generated I_3^- species with time.^[56, 57]

2.2.6.2 Raman Spectroscopy under Applied Potential

Operando Raman spectro–electrochemical studies were carried out in a similar three-electrode system to elucidate the electrochemical reaction between the poly-iodides of the electrolyte (such as I_3^- , I_5^-) and the COF. All Raman spectra are collected in a confocal geometry with a 532 nm excitation laser (2 mW), which was focused on the surface of the COF-pellet pressed on an ITO plate. No additional mechanical binder or electrically conductive additive was required since the pellet was directly pressed on the surface of the electrically conductive ITO plate to form the electrode (Figure A.2.31.). Thereby all possible sources of stray signals were avoided. Pristine COF exhibits the standard vibrational bands at $\nu(C=C)$: 1590 cm^{-1} , $\nu(C=O)$: 1610 cm^{-1} , and $\nu(C=N)$: 1665 cm^{-1} originating from the aromatic in-plane tangential mode.^[58-62] The presence of a delocalized charge density and extensive π -stacking is characterized by the sharp vibrational modes (FWHM $<20\text{ cm}^{-1}$) observed in the case of the pristine COF. The lower frequency region ($75\text{ to }800\text{ cm}^{-1}$) did not exhibit any strong vibrational mode for the pristine COF (Figure 2.13.B(i,ii); Figures A.2.32. and A.2.33.; Table A.2.8.). Interestingly, new Raman bands were observed under the influence of a threshold electrode potential of 0.8 V during chronoamperometry. The dominant role of I_3^- is confirmed by the emergence of bands at $226\text{ and }332\text{ cm}^{-1}$, which correspond to the $2\nu_1$ and $3\nu_1$ (fundamental overtones) of polyiodide species I_3^- . The bands at $300\text{ and }600\text{ cm}^{-1}$ are unambiguously assigned to the formation of a polar bond between the COF and I_3^- .^[19, 63-65] Accordingly, the 300 cm^{-1} band is attributed to the direct bond formation between COF and iodine (C-I stretch). The band at 600 cm^{-1} is an overtone of the C-I bond and is prominent only above a threshold potential difference of 0.8 V.^[64] Further, the effect of such iodination of the COF is also reflected as the splitting of the aromatic C=C ring stretch due to the π - π^* - I_3^- charge-transfer induces symmetry-breaking, in agreement with the XPS results (vide infra). Finally, the electrochemically driven nature of this reaction is reaffirmed by the absence of all these features below 0.8 V by chronopotentiometric measurements, too (Figure 2.13. B(ii); Figures A.2.32. and A.2.33.; Table A.2.8.). Importantly, the entire bond-formation is reversed by the removal of the applied potential, indicating excellent reversibility of the pseudo-capacitive reaction.

2.2.7. X-Ray Photoelectron Spectroscopy

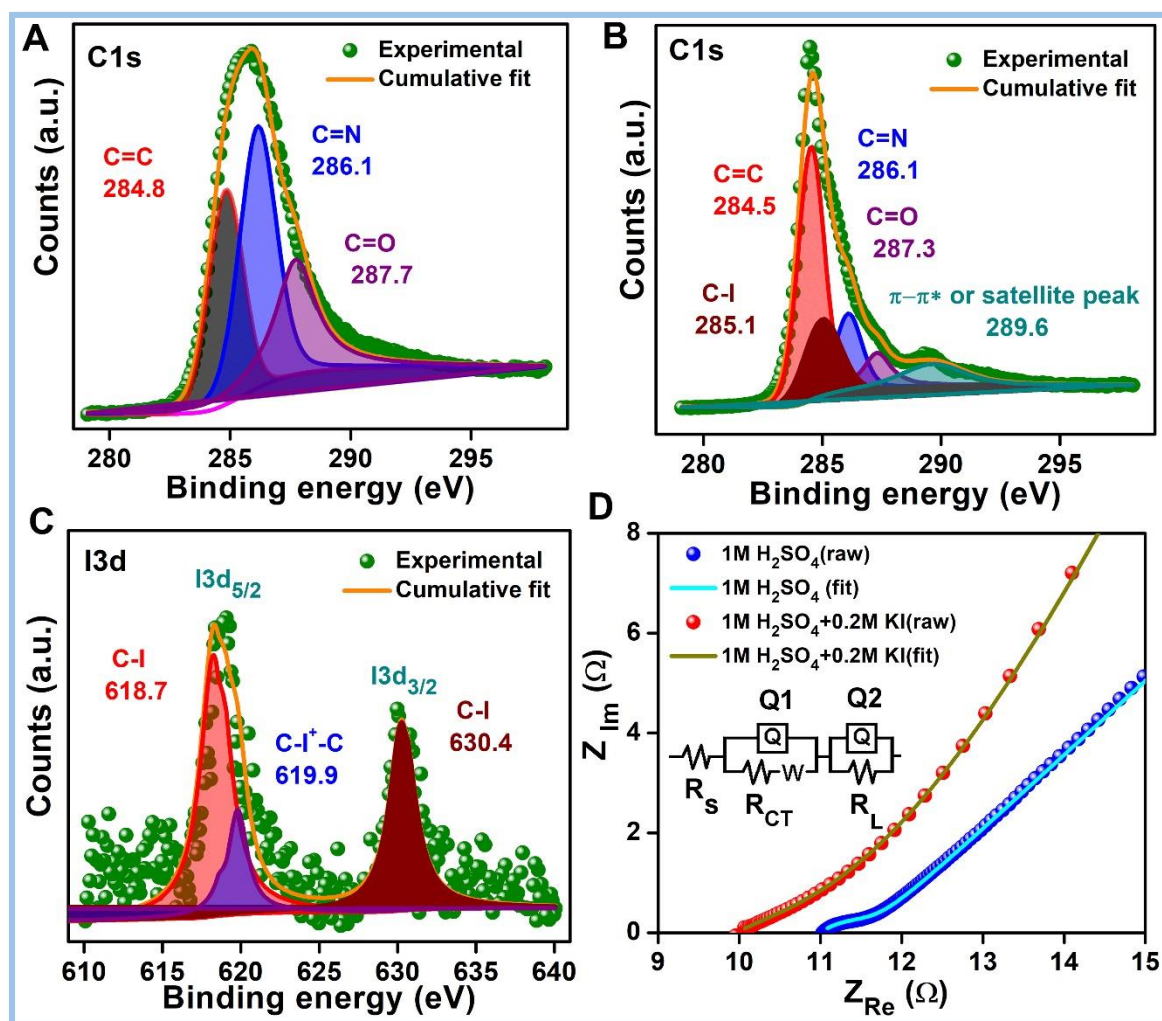


Figure 2.14. Comparison of the XPS. A) C1s spectra of neat COF versus B) C1s spectra of completely charged (iodized) electrode. C) shows the I3d level spectra of the charged COF-electrode. D) Nyquist plots from the impedance measurements made on the COF-derived solid-state device, the fit is obtained using an equivalent circuit $R(Q(RW))(QR)$ shown in the inset. The values of circuit elements can be found in the Appendix chapter 2.

XPS was appropriated to investigate the constituents generated during the redox process on the completely charged electrode's surface. The deconvoluted C1s spectrum has peaks at 284.5, 286.1, and 287.3 eV arising due to the C=C, -C=N (Schiff bonds and triazine) and C=O bond along with an extra peak at 285.1 eV, which could be due to the formation of C-I during oxidation at the electrode surface (Figures 2.14. A,B; Figures A.2.34. and A.2.35.).^[63] Compared to the neat COF, the polyiodide adsorbed COF shows a narrow FWHM near 285 eV (3.3 for COF versus 1.5 eV for $I_3^-@COF$), which is an indication that the species is

dominated by 284.5 eV (-C=C) and 285.1 eV (C-I species). The peak maximum shifts from 285.8 eV (neat COF) to ≈ 284.5 eV (in KI) after the iodide modification in COF. Thus, the narrowing of FWHM and shift in peak maxima toward 285.0 eV indicates the change in C-environment created by the interaction with the iodide species. A satellite peak at 289.6 eV confirms the π - π^* charge transfer between the layers or between the polyanionic and some cationic defects.^[66, 67] In the case of I 3d, two peaks at 618.7 (I 3d_{5/2}) and 630.4 eV (I 3d_{3/2}) states confirm the formation of C-I during the oxidation process (Figures 2.14. C and A.2.35.).^[27, 68] The signals from I 3d_{5/2} at 619.9 eV correspond to the interaction between carbon and iodine species in the bridging fashion as C-I+-C.^[69] It could be the interlayer bridge or the between two consecutive sp² carbon of benzene ring with oxidation products of I⁻ during the reaction process. This cationic species could easily facilitate the charge transfer between some polyiodide species such as I₃⁻ or I₅⁻ etc.

2.2.8. Impedance Spectroscopy of the Solid-State Device

The impedance spectroscopy measurements using the solid-state capacitor reveals a sizable lowering of resistance upon switching the electrolyte from H₂SO₄ (aq) to H₂SO₄ (aq) + KI. The impedance plots were fitted using the same equivalent circuit used for three-electrode impedance fits (Figure 2.14. D and Table A.2.9). Both the ohmic resistance (R_s) and the charge transfer resistance (R_{CT}) decrease upon the inclusion of KI. The diffusion characteristics have been analyzed through a plot of Z' against $\omega^{-1/2}$ (Figure A.2.36). The resulting linear fit yields a slope (Warburg constant) of $2.9 \omega^{-1/2}$ for the composite in the redox electrolyte and $3.8 \omega^{-1/2}$ in neat acid. This indicates that the diffusion kinetics is slower for the former, which is expected considering the bulkiness of the I₃⁻ compared to H⁺. This slow-diffusion of the redox electrolyte over the neat acid compares well with our observations from three-electrode AC-impedance measurements in the liquid state. Thus, the KI, as an active redox additive, plays a favorable role in lowering the overall resistance. In addition to the I₃⁻, the participation of I₂ in reducing the electrode–electrolyte interface resistance cannot be neglected.^[65, 70] This lowering of resistance could be due to improved bulk wettability caused by polyiodide inclusion. Or it could genuinely be molecular in origin (polarizing COF backbone allures polarizable polyiodide). To verify this, the contact angles for different solvents were measured. The COF's contact angle values for water, toluene, 1M H₂SO₄ (aq), and the solution containing 0.2M KI + 1M H₂SO₄ (aq) were measured. Interestingly, the bulk COF was highly amphiphilic; it readily absorbs water, toluene, methanol, ethanol, H₂SO₄ and H₂SO₄ + KI both in powder and

pellet form, which is quite different from some of our earlier reported COFs.^[71,72] This property could add advantageously to the wettability of the COF when employed as an electrode with aqueous redox electrolytes. It aids the ionic transport at the electrode–electrolyte interface and can thereby enhance the capacitance. But would not differentiate between the highly wetting H_2SO_4 and $\text{H}_2\text{SO}_4 + \text{KI}$. This would mean the superior interaction of the COF with the polyiodide is more at a molecular level than a mere bulk phenomenon. Given that many highly stable gel-based solid-state charge storage devices employ polymeric organic materials, our findings with KI could be widely beneficial.

2.2.9. Role of Different Components of the Composite-Electrode toward Capacitance Building

To further investigate each component's role in gaining large capacitance in the redox electrolyte system, we carried out a series of control experiments. All CVs were measured using a three-electrode configuration by employing the control-coated on Toray carbon paper ($1\text{ cm} \times 1\text{ cm}$) geometrical area as the working electrode. The results are shown in Figure 2.15. A comparison of the CVs in only H_2SO_4 of the neat COF, carbon, and the composite reveals the composite's superior performance over the others. Importantly, the neat carbon shows only an archetypal EDLC behavior while the neat COF shows EDLC + minor pseudo activity. A measurement of their electronic conductivity using a four-probe set-up showed that the composite gains substantial electronic activity from just 15% carbon addition (IISERP-COF25 = $3.2 \times 10^{-4}\text{ S cm}^{-1}$; Super P carbon = $1.5 \times 10^1\text{ S cm}^{-1}$; Composite (80% COF + 15% carbon + 5% Nafion) = $7.3 \times 10^{-1}\text{ S cm}^{-1}$). This carbon most likely activates the COF in the electrolyte system. The conductivity of carbon in the composite facilitates the flow of electrons and thereby the redox reactions, without which the electrons would have merely accumulated on the surface of the COF. The capacitance contribution coming from the 15% carbon in the composite of active material is negligible. The composite in the $\text{H}_2\text{SO}_4 + \text{KI}$ system shows a non-linear GCD owing to significant pseudo activity, as would be expected from the CV (from 0.4 to 0.8 V). However, the pseudo activity at each functional group of the COF (in the composite) could not be partitioned as their interactions occur at closely placed potentials, as seen from the CV. The neat Super P carbon, in the redox electrolyte shows much lower discharge times GCD (Figure A.2.26.). This shows that the COF-carbon certainly operates as a better charge-storage system.

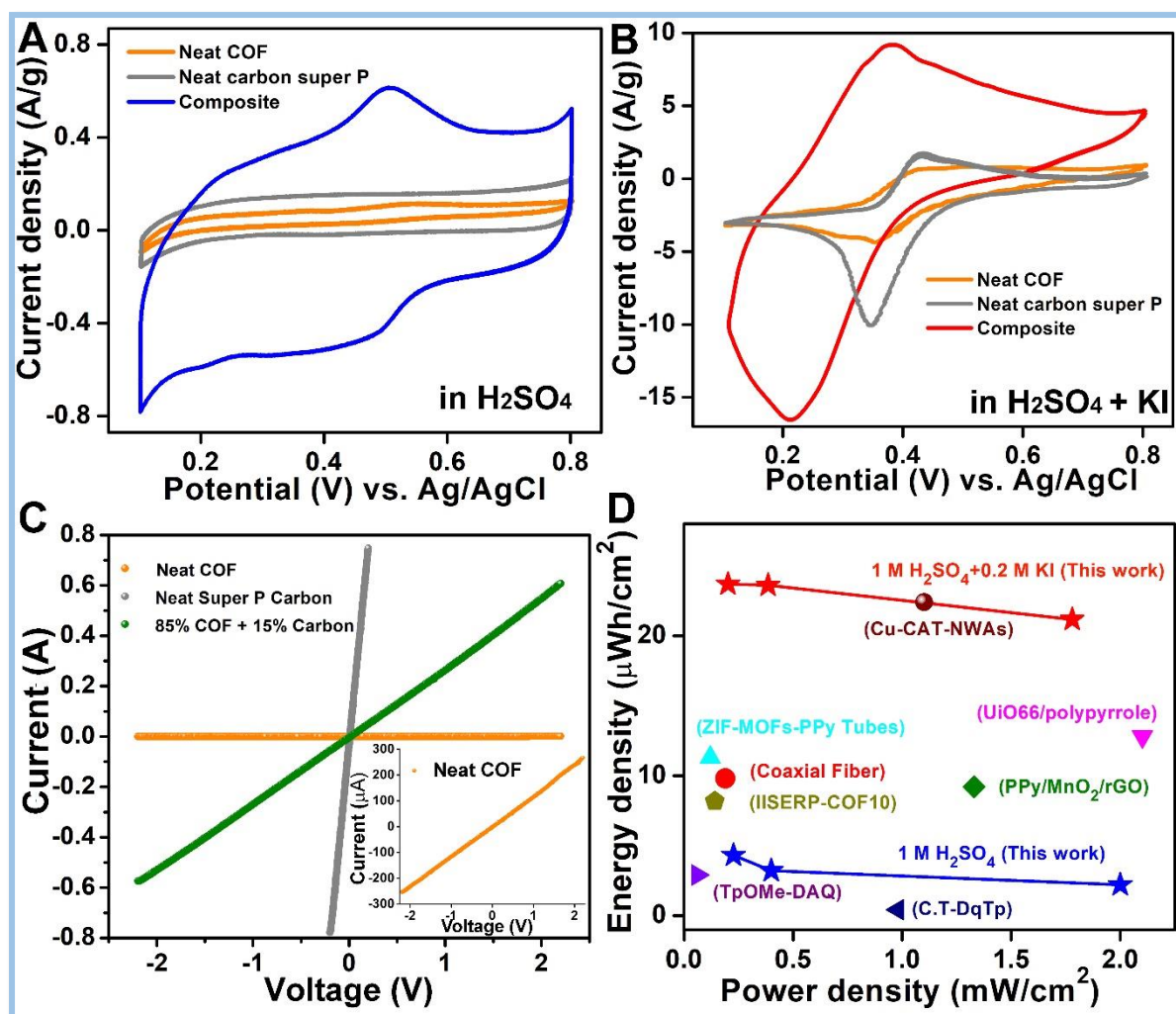


Figure 2.15. (A) All CVs shown in this figure have been measured in a three-electrode assembly @ 2 mV s⁻¹ scan rate with 2 mg loading of composite, using Toray carbon paper as working electrode A) CV plots of the neat COF versus super P carbon versus the composite measured using 1M H₂SO₄ as an electrolyte. (B) Comparative CV plots of the neat COF versus super P carbon versus the composite measured independently using 1M H₂SO₄ + 0.2M KI as an electrolyte. (C) Comparative I–V plots of the COF, carbon, and the composite performed using a four-probe conductivity set-up. The electronic conductivity imparted to the poorly conducting COF by the carbon is seen. Conductivity at 60 °C: IISERP-COF = 3.2×10^{-4} S cm⁻¹; super P carbon = 1.5×10^1 S cm⁻¹; Composite (80% COF + 15% carbon + 5% Nafion) = 7.3×10^{-1} S cm⁻¹. (D) The Ragone plot is based on geometrical areal energy and power densities comparison with the top-performing MOF and COF fabricated electrodes.

Another control experiment done using K₂SO₄ (Figure A.2.14.) in place of KI showed no enhancement in the capacitance of the composite in the K⁺ + H₂SO₄ electrolyte, which further confirms that the majority of the capacitance enhancement comes from the polyiodide species generated by the KI in H₂SO₄ electrolyte. In summary, an excellent synergy between COF and

the conducting carbon in the redox electrolyte sets up the scene leading to ≈ 6.5 times enhancement of areal capacitance and ≈ 8 times enhancement in gravimetric specific capacitance of the otherwise dull COF system (Figure 2.15A–C). A Ragone plot captures the superior performance of this IISERP-COF25-derived electrode compared to other related systems (Figure 2.15D).^[9, 30, 35, 73-79]

A systematic variation of the loading of active material in the solid-state device showed that with increasing loading, the areal capacitance increases, meanwhile, the gravimetric capacitance does drop (Figures A.2.45.– A.2.47. and Table A.2.10). This was consistent across multiple devices. This would mean at higher loadings, there is a significant amount of dead material (the material that does not make proper contact with the current collector) contributing only to the internal resistance. A pertinent report from Eddaoudi and coworkers on RuO₂-COF-based asymmetric capacitors shows excellent energy (23.3 Wh kg^{-1}) and power density (661.2 W kg^{-1}).^[80] The asymmetric capacitor configuration and the use of relatively dense RuO₂ as a redox component enable them to deliver this high energy density at a potential as high as 1.7 V. In comparison; we present a much inexpensive redox system (polyiodide). Similarly, exfoliated COF has been engineered as thinner electrodes to achieve high areal capacitance and power densities.^[81] Thus, an asymmetric configuration coupled with a better-contrived electrode geometry could aid COF to reach higher voltages leading to excellent capacitor performances.

2.2.10. Charge-Storage Mechanism of the COF-Carbon Composite

The charge storage mechanism of our COF-based supercapacitor could be explained like this. First of all, the iodide ions present on the surface of the working electrode is converted to I₂ by the electrochemical oxidation process or by direct oxidation in the acidic medium, then I₂ interacts with material coated on the working electrode as well as with the bulk electrolyte, these surfaces aid their clustering and nucleate them to grow as polyiodides such as I₃[−]. I₂ can also interact with the acidic electrolyte to form IO₃[−]. As a crucial step, the conducting carbon of the composite activates the different interaction sites in the COF (triazine and phenyl rings). Simultaneously, the protons are known to activate the Schiff bonds and induce keto-enol tautomerism at the oxygen sites. Such sites are excellent redox-active centers for the incoming iodine/iodide species to interact. Additionally, when the relatively large polyiodide ions decorate the surfaces and pore walls of the COF and the carbon, they make them more inundated, leading to an increased surface area. Such an interface becomes excellent to promote

further EDLC sites for incoming protons. Since the nano-confinement of the COF pores offers a more stabilizing “potential well,” the surface adsorbed polyiodides diffuse into the pores of the electrodes to participate in redox reactions.^[36] As well, the protons in the electrolyte can protonate the COF's framework leaving an ionized polarizing wall; such an environment renders these COF pores as polyiodide absorbing “*molecular-sponges*.” Thus adsorbed anionic polyiodide species get activated/polarized in the pores and serve as additional sites for more protons to adsorb. This is how protons and the polyiodides could synergistically enhance each other's adsorption based storage. This proton–polyiodide synergy is affirmed using computational modeling (discussed later in the text).

2.3. Cyclic Stability of the COF under the Highly Reactive Iodide-Rich Electrolyte Medium

To ascertain the COF's stability in this relatively harsh electrolyte, we subjected the COF-derived composite to 10,000 cycles in a three-electrode configuration. For this, the composite was coated on a large surface (4 cm × 2 cm) Pt mesh was used as the working electrode (Figure 2.16.). The post-CV sample was characterized using PXRD, HRTEM, XPS, and IR spectroscopy.

Stability of the composite-electrode subjected to multiple cycles CV:

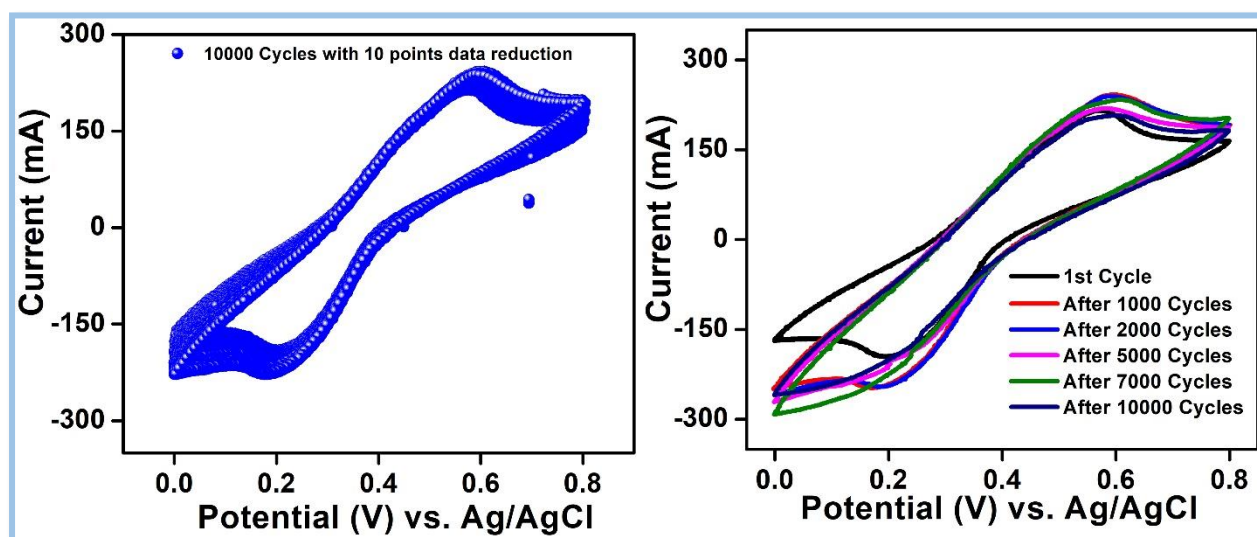


Figure 2.16. (A) CV measurements @100 mV/s using platinum mesh electrode as a working electrode coated with the composite (80% IISERP-COF25+ 15% Super P carbon) in H₂SO₄ + KI electrolyte system. (B) CVs @100 mV/s after a different number of cycles.

The PXRD comparisons revealed a significant lowering of crystallinity when subjected to 10 000 cycles (Figure 2.17.A). Notably, the resulting powder was insoluble in water or any organic solvents suggestive of its polymeric structure. It shows peaks corresponding to C-I interactions in the XPS (Figure 2.17.B and Figure A.2.49.), which compare well with the peaks observed in the XPS spectrum of the composite subjected to fewer cycles (Figure 2.14.).

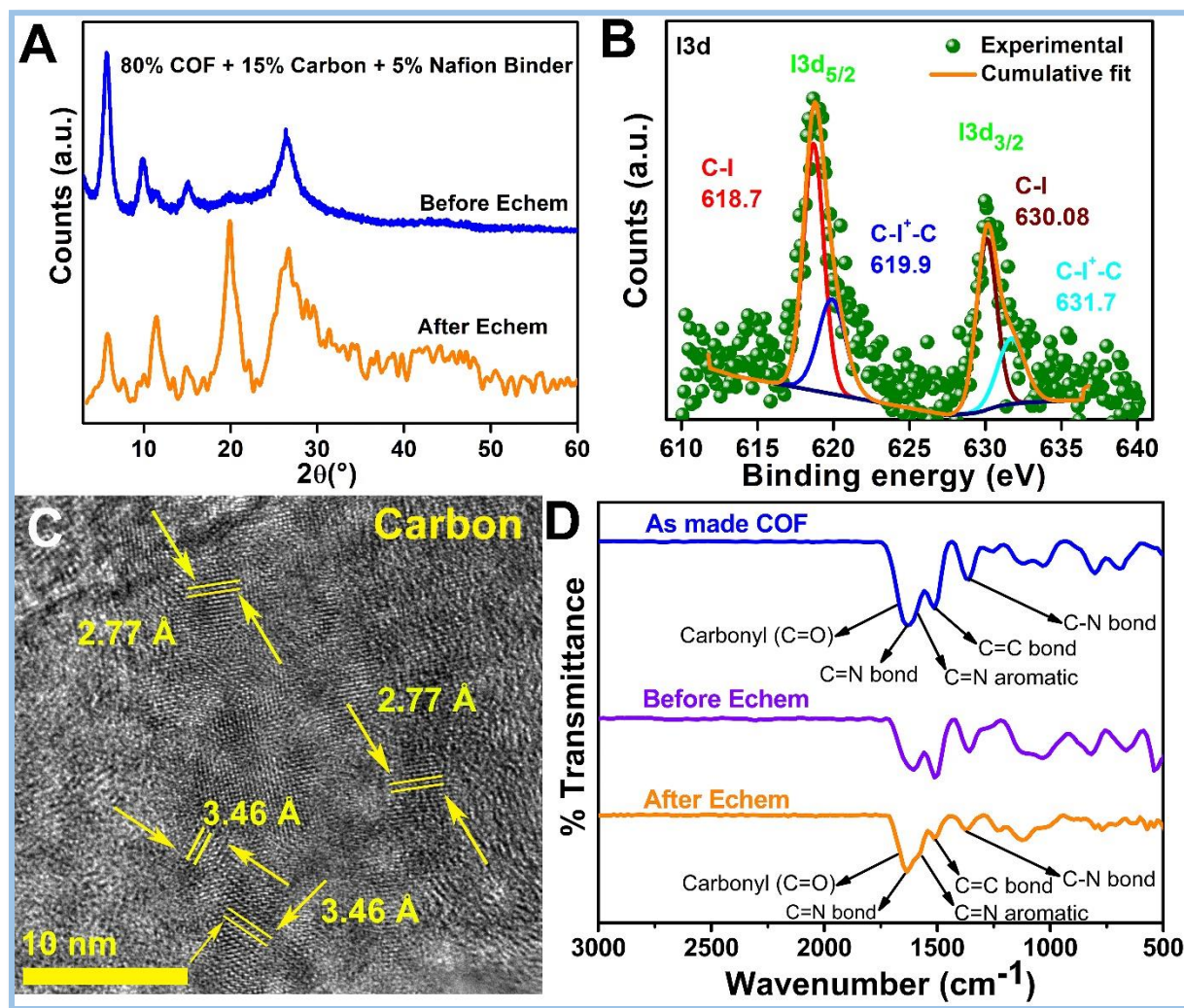


Figure 2.17. (A) A comparative PXRD pattern of the composite before and after subjecting to 10,000 cycles using 1M H₂SO₄ + 0.2M KI as the electrolyte. (B) I3d XPS spectra of Composite material after 10,000 cycles. (C) HRTEM images of the composite subjected to 10,000 cycles showing the lattice fringes from the crystalline COF flakes. The presence of carbon flakes on the COF surface could also be observed. (D) Comparative IR spectra of the pre-and post-cycling composite showing functional group preservation.

The HRTEM images of these 10000 cycled samples still displayed some crystalline flakes with lattice fringes (Figure 2.17.C and Figure A.2.50.), though the d-spacing of 3.46 Å agrees well

with those observed for the as-synthesized COF (interlayer spacing), the exposing of new lattice fringes from a different facet (d-spacing of 2.77 Å) suggests structural changes caused by the prolonged cycling. However, only a few such flakes could be observed compared to a sample subjected only to 700 cycles (Figures A.2.51. and A.2.52.). In summary, though the polymeric structure is retained over 10,000 cycles, the crystallinity of the composite electrode is lowered, which partly explains the drop in capacitance with prolonged cycling (Figure 2.12.D). Meanwhile, the IR spectra show peaks resembling those surveyed for the as-made COF, confirming the intactness of functional groups and linkages (Figure 2.1.7D).

2.4. Computational Modeling

The redox electrolyte employed here can generate a range of polyiodides, which form as dynamic species under an applied potential and get adsorbed into COF pores and give rise to Faradaic redox reactions. To verify the stability of the polyiodide-COF structures and to understand their molecular-level interactions, we resorted to computational modeling.^[82]

2.4.1. Interaction of I_3^- , I^- , I_2 , and H_3O^+ with the COF under an External Electric Field

Based on results from the spectro-electrochemistry, I_3^- was considered to be the dominant species capable of interacting with the protonated COF. A Grand Canonical Monte Carlo (GCMC) calculation and the structural optimization were performed using the Simulated Annealing routine embedded in the Materials Studio V8. The stable low-energy configuration with two I_3^- per unit-cell was chosen as the initial model. This unit cell was subjected to an external isotropic field of 0.05 eV Å⁻¹/e using the CASTEP routine and a stable final geometry-optimized structure with acceptable Vander Waals distances and bond lengths were obtained.^[83, 84]

The optimized structure has a total energy of -10 691 eV per unit-cell and displays a contracted unit cell in the triclinic space group with lattice parameters shown in Figure 2.18. This suggests a potential driven, dynamic framework flexibility.^[83] In this configuration, the polyiodides orient parallel to the wall resembling I_3^- trapped in Cyclodextrin.^[36] The micropores offer sufficient room for the polyiodides, and some of the I_3^- reside proximal to the framework wall (COF... I_3^- : 3.66 Å) while the other rested closer to the protonated water molecules. The iodide closer to the water molecules get highly polarized and has a longer I-I bond length (2.81 Å)

and they take a bent structure significantly deviating from the ideal $\angle \text{I-I-I} = 180^\circ$).^[36] The distances between the I_3^- units and the framework atoms (3.66–4.27 Å) are in the physisorptive range, which explains the observed reversibility in the polyiodide storage (Figure 2.18.B). It is essential to note that the energy dispersive X-ray analysis (EDAX) of the sample washed after the electrochemical run shows the presence of iodine-based species but no potassium trace (Figures A.2.41.–A.2.44.).

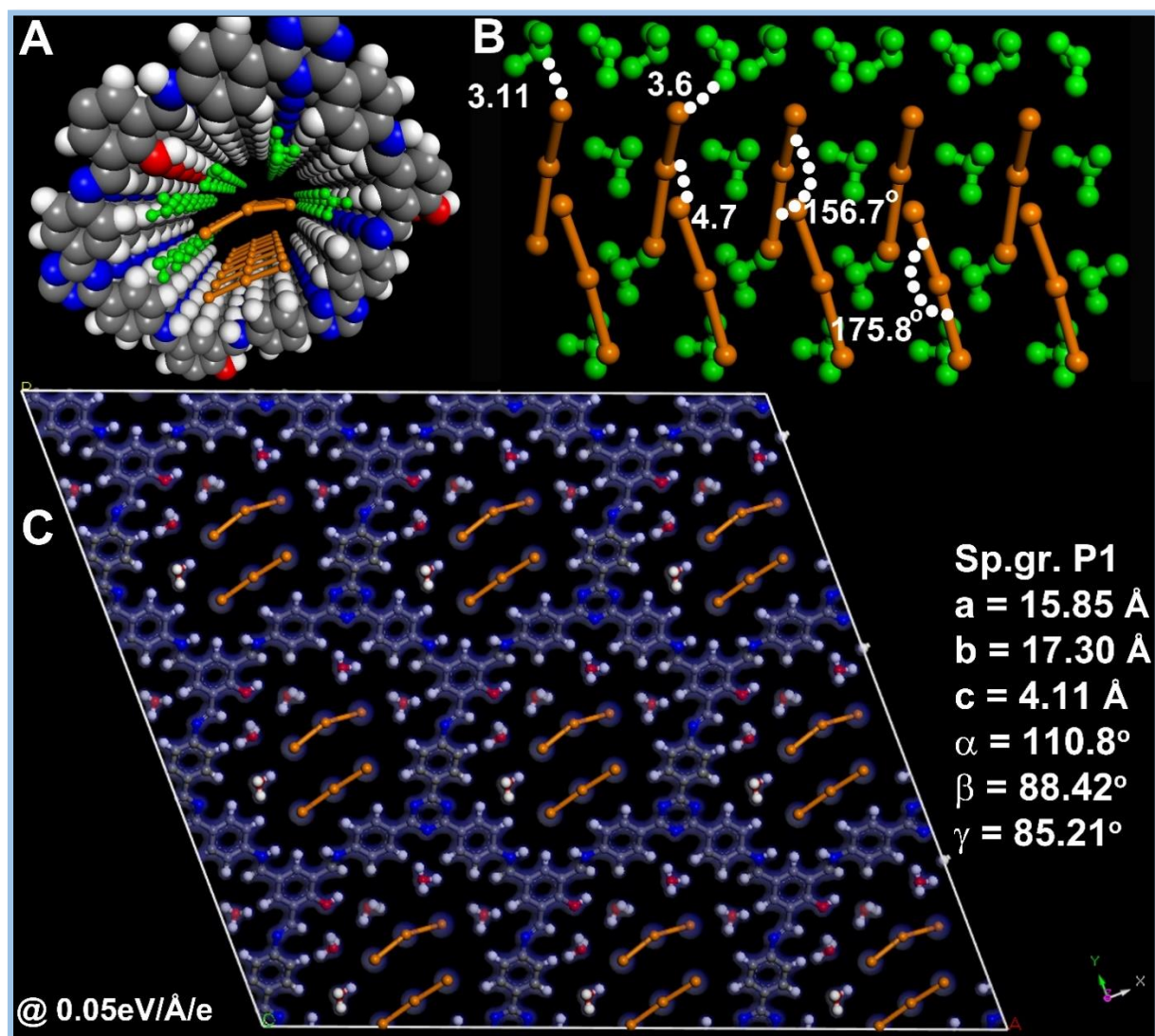


Figure 2.18. (A) A single channel from the modeled structure with H_3O^+ and I_3^- in the pores of the COF framework optimized under an external electric potential. For clarity, the H_3O^+ ions are shown in green only in (A and B). (B) Figure Shows the orientation of the I_3^- and H_3O^+ and some of the shortest distances between them. (C) A Connolly surface representation of the (Grid size: 0.15, Probe radius: 0.4 Å) showing the proximity of the free ions to the framework walls. Color code: I-orange; N-blue; O-red; C-grey; H-white.

This would mean the anionic iodides participate in charge-balancing the protonated COF framework and do not exist as mere salt (KI or K₂SO₄). Similar optimizations were carried out for I₂ and I⁻ under the same applied external field. Their relative energy comparisons reveal that the structure hosting I₃⁻ ions show the lowest relative energy than the COF containing I₂, I⁻ and H₃O⁺ species (Figure A.2.53.). Markedly, all the optimized-structures having these Iodine-derived species confined in the COF nanopores have acceptable energies (Figure A.2.53.).

2.5. Conclusion

The work conveys the drastic enhancement of capacitive storage of a crystalline porous polymer when coupled with a redox electrolyte and conducting carbon. Detailed spectro-electrochemical investigations on the neat COF in redox electrolyte supported by XPS point to the manifestation of in situ generated anionic polyiodide species. Electrochemical measurements confirm their Faradaic and EDLC type interactions with the COF-carbon electrodes. Meanwhile, such polyiodide species' influence in lowering charge-transfer and bulk resistance is perceived from the impedance analysis. Thus, we find COF with ordered pores and “polarizing pore-walls” offers favorable diffusion space and redox-activity for the “polarizable” polyiodides, not undermining the electronic contribution provided by the conducting carbon additive. We have reasons to believe that the extent to which these COF can respond to the redox-active electrolytes can be further tuned by modulating their texture, morphology, and sono-mechanical properties and by adopting an asymmetric capacitor mode. For this, a detailed systematic investigation employing a library of COF-derived systems is underway.

2.6. Acknowledgements

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2.7. References:

- [1] Q. Meng, K. Cai, Y. Chen, L. Chen, *Nano Energy* 2017, 36, 268.
- [2] I. Shown, A. Ganguly, L. C. Chen, K. H. Chen, *Energy Sci. Eng.* 2015, 3, 2.
- [3] M. Wang, H. Guo, R. Xue, Q. Li, H. Liu, N. Wu, W. Yao, W. Yang, *ChemElectroChem* 2019, 6, 2984.
- [4] G. G. Prasad, N. Shetty, S. Thakur, K. Bommegowda, *IOP Conf. Ser.: Mater. Sci. Eng.* 2019, 561, 012105.
- [5] F. Wang, X. Wu, X. Yuan, Z. Liu, Y. Zhang, L. Fu, Y. Zhu, Q. Zhou, Y. Wu, W. Huang, *Chem. Soc. Rev.* 2017, 46, 6816.
- [6] C. R. DeBlase, K. Hernández-Burgos, K. E. Silberstein, G. G. Rodríguez-Calero, R. P. Bisbey, H. D. Abruña, W. R. Dichtel, *ACS Nano* 2015, 9, 3178.
- [7] F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu, D. Jiang, *Angew. Chem., Int. Ed.* 2015, 54, 6814.
- [8] M. S. Lohse, T. Bein, *Adv. Funct. Mater.* 2018, 28, 1705553.
- [9] A. Halder, M. Ghosh, A. Khayum M, S. Bera, M. Addicoat, H. S. Sasmal, S. Karak, S. Kurungot, R. Banerjee, *J. Am. Chem. Soc.* 2018, 140, 10941.
- [10] J. Xu, Y. He, S. Bi, M. Wang, P. Yang, D. Wu, J. Wang, F. Zhang, *Angew. Chem.* 2019, 131, 12193.
- [11] C. R. DeBlase, K. E. Silberstein, T.-T. Truong, H. c. D. Abruña, W. R. Dichtel, *J. Am. Chem. Soc.* 2013, 135, 16821.
- [12] P. Bhanja, K. Bhunia, S. K. Das, D. Pradhan, R. Kimura, Y. Hijikata, S. Irle, A. Bhaumik, *ChemSusChem* 2017, 10, 921.
- [13] A. M. Khattak, Z. A. Ghazi, B. Liang, N. A. Khan, A. Iqbal, L. Li, Z. Tang, *J. Mater. Chem. A* 2016, 4, 16312.
- [14] B. Sun, J. Liu, A. Cao, W. Song, D. Wang, *Chem. Commun.* 2017, 53, 6303.
- [15] Z. Zha, L. Xu, Z. Wang, X. Li, Q. Pan, P. Hu, S. Lei, *ACS Appl. Mater. Interfaces* 2015, 7, 17837.

- [16] Y. Wu, D. Yan, Z. Zhang, M. M. Matsushita, K. Awaga, ACS Appl. Mater. Interfaces 2019, 11, 7661.
- [17] C. R. Mulzer, L. Shen, R. P. Bisbey, J. R. McKone, N. Zhang, H. c. D. Abruña, W. R. Dichtel, ACS Cent. Sci. 2016, 2, 667.
- [18] S. Liu, L. Yao, Y. Lu, X. Hua, J. Liu, Z. Yang, H. Wei, Y. Mai, Mater. Lett. 2019, 236, 354.
- [19] E. Frackowiak, M. Meller, J. Menzel, D. Gastol, K. Fic, Faraday Discuss. 2014, 172, 179.
- [20] S. Sundriyal, V. Shrivastav, M. Sharma, S. Mishra, A. Deep, Chemis-trySelect 2019, 4, 2585.
- [21] L.-Q. Mai, A. Minhas-Khan, X. Tian, K. M. Hercule, Y.-L. Zhao, X. Lin, X. Xu, Nat. Commun. 2013, 4, 2923.
- [22] M. Meller, J. Menzel, K. Fic, D. Gastol, E. Frackowiak, Solid State Ionics 2014, 265, 61.
- [23] S. Senthilkumar, R. K. Selvan, Y. Lee, J. Melo, J. Mater. Chem. A 2013, 1, 1086.
- [24] S. Roldán, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, Angew. Chem., Int. Ed. 2011, 50, 1699.
- [25] S. Roldán, M. Granda, R. Menéndez, R. Santamaría, C. Blanco, J. Phys. Chem. C 2011, 115, 17606.
- [26] S. Roldán, M. Granda, R. Menéndez, R. Santamaría, C. Blanco, Elec-trochim. Acta 2012, 83, 241.
- [27] K. Jayaramulu, D. P. Dubal, B. Nagar, V. Ranc, O. Tomanec, M. Petr, K. K. R. Datta, R. Zboril, P. Gómez-Romero, R. A. Fischer, Adv. Mater. 2018, 30, 1705789.
- [28] B. Nagar, D. P. Dubal, L. Pires, A. Merkoçi, P. Gómez-Romero, ChemSusChem 2018, 11, 1849.
- [29] Y. Li, X. Zhao, Q. Xu, Q. Zhang, D. Chen, Langmuir 2011, 27, 6458.
- [30] S. Halder, R. Kushwaha, R. Maity, R. Vaidhyanathan, ACS Mater. Lett. 2019, 1, 490.
- [31] A. P. Cote, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, Science 2005, 310, 1166.

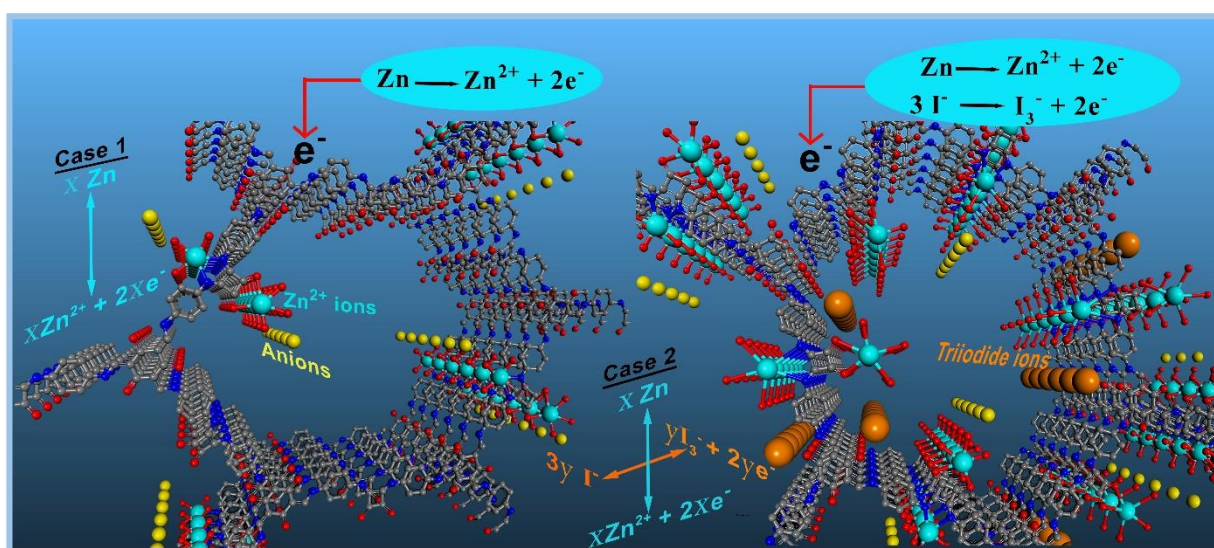
- [32] D. Chakraborty, S. Nandi, D. Mullangi, S. Haldar, C. P. Vinod, R. Vaidhyanathan, *ACS Appl. Mater. Interfaces* 2019, 11, 15670.
- [33] S. Haldar, K. Roy, S. Nandi, D. Chakraborty, D. Puthusseri, Y. Gawli, S. Ogale, R. Vaidhyanathan, *Adv. Energy Mater.* 2018, 8, 1702170.
- [34] S. Haldar, K. Roy, R. Kushwaha, S. Ogale, R. Vaidhyanathan, *Adv. Energy Mater* 2019, 9, 1902428.
- [35] A. Khayum M, V. Vijayakumar, S. Karak, S. Kandambeth, M. Bhadra, K. Suresh, N. Acharambath, S. Kurungot, R. Banerjee, *ACS Appl. Mater. Interfaces* 2018, 10, 28139.
- [36] J. W. Minns, A. Khan, *J. Phys. Chem. A* 2002, 106, 6421.
- [37] N. U. Day, M. G. Walter, C. C. Wamser, *J. Phys. Chem. C* 2015, 119, 17378.
- [38] B.-A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, *J. Phys. Chem. C* 2018, 122, 194.
- [39] R. Raccichini, L. Furness, J. W. Diben, J. R. Owen, N. Garcia-Araez, *J. Electrochem. Soc.* 2018, 165, A2741.
- [40] S. Fletcher, *J. Chem. Soc., Faraday Trans.* 1993, 89, 311.
- [41] W. Wang, S. Guo, I. Lee, K. Ahmed, J. Zhong, Z. Favors, F. Zaera, M. Ozkan, C. S. Ozkan, *Sci. Rep.* 2014, 4, 4452.
- [42] C. Masarapu, H. F. Zeng, K. H. Hung, B. Wei, *ACS Nano* 2009, 3, 2199.
- [43] S. M. Poljacek, D. Risovic, T. Cigula, M. Gojo, *J. Solid State Electro-chem.* 2012, 16, 1077.
- [44] L.-Q. Mai, A. Minhas-Khan, X. Tian, K. M. Hercule, Y.-L. Zhao, X. Lin, X. Xu, *Nat. Commun.* 2013, 4, 2923.
- [45] H. Gul, A.-u.-H. A. Shah, S. Bilal, *Polymers* 2019, 11, 1678.
- [46] D. C. Apodaca, R. B. Pernites, R. Ponnampati, F. R. Del Mundo, R. C. Advincula, *Macromolecules* 2011, 44, 6669.
- [47] A. Inayat, S. Bilal, *Catalysts* 2019, 9, 631.
- [48] M. H. de Araujo, T. Matencio, C. L. Donnici, H. D. R. Calado, *Polimeros* 2020, 30, e2020001.

- [49] S. Zhao, F. Wu, L. Yang, L. Gao, A. F. Burke, *Electrochem. Commun.* 2010, 12, 242.
- [50] S. Zhao, Y. Li, H. Yin, Z. Liu, E. Luan, F. Zhao, Z. Tang, S. Liu, *Sci. Adv.* 2015, 1, e1500372.
- [51] Z. Weng, Y. Su, D. W. Wang, F. Li, J. Du, H. M. Cheng, *Adv. Energy Mater.* 2011, 1, 917.
- [52] W. Zhou, K. Zhou, X. Liu, R. Hu, H. Liu, S. Chen, *J. Mater. Chem. A* 2014, 2, 7250.
- [53] S. Halder, D. Chakraborty, B. Roy, G. Banappanavar, K. Rinku, D. Mullangi, P. Hazra, D. Kabra, R. Vaidhyanathan, *J. Am. Chem. Soc.* 2018, 140, 13367.
- [54] X. Li, Q. Gao, J. Wang, Y. Chen, Z.-H. Chen, H.-S. Xu, W. Tang, K. Leng, G.-H. Ning, J. Wu, *Nat. Commun.* 2018, 9, 2335.
- [55] H. Ding, J. Li, G. Xie, G. Lin, R. Chen, Z. Peng, C. Yang, B. Wang, J. Sun, C. Wang, *Nat. Commun.* 2018, 9, 52341.
- [56] R. Baldwin, R. Bear, R. Rundle, *J. Am. Chem. Soc.* 1944, 66, 111.
- [57] M. Savastano, C. Bazzicalupi, C. García, C. Gellini, M. D. L. de la Torre, P. Mariani, F. Pichierri, A. Bianchi, M. Melguizo, *Dalton Trans.* 2017, 46, 4518.
- [58] D. Chakraborty, S. Nandi, R. Illathvalappil, D. Mullangi, R. Maity, S. K. Singh, S. Halder, C. P. Vinod, S. Kurungot, R. Vaidhyanathan, *ACS Omega* 2019, 4, 13465.
- [59] H. Liu, Q. Li, Y. Zhu, M. Zhang, R. Liu, X. Li, X. Kang, Z. Li, S. Qiao, *J. Mater. Chem. C* 2018, 6, 722.
- [60] T. Jadhav, Y. Fang, W. Patterson, C. H. Liu, E. Hamzehpoor, D. F. Perepichka, *Angew. Chem., Int. Ed.* 2019, 58, 13753.
- [61] M. K. Jha, R. Ball, R. Seelaboyina, C. Subramaniam, *ACS Appl. Energy Mater.* 2020, 3, 3454.
- [62] M. K. Jha, K. Hata, C. Subramaniam, *ACS Appl. Mater. Interfaces* 2019, 11, 18285.
- [63] S. Some, J. S. Sohn, J. Kim, S.-H. Lee, S. C. Lee, J. Lee, I. Shackery, S. K. Kim, S. H. Kim, N. Choi, *Sci. Rep.* 2016, 6, 20015.
- [64] S. C. O'Brien, C. Kittrell, J. L. Kinsey, B. R. Johnson, *J. Chem. Phys.* 1992, 96, 67.

- [65] Y. Zhao, J. Wei, R. Vajtai, P. M. Ajayan, E. V. Barrera, *Sci. Rep.* 2011, 1, 83.
- [66] X. H. Yang, J. W. Guo, S. Yang, Y. Hou, B. Zhang, H. G. Yang, *J. Mater. Chem. A* 2014, 2, 614.
- [67] V. Vij, J. N. Tiwari, W.-G. Lee, T. Yoon, K. S. Kim, *Sci. Rep.* 2016, 6, 20132. [68] G. Zhang, M. Zhang, X. Ye, X. Qiu, S. Lin, X. Wang, *Adv. Mater.* 2014, 26, 805.
- [69] Q. Han, C. Hu, F. Zhao, Z. Zhang, N. Chen, L. Qu, *J. Mater. Chem. A* 2015, 3, 4612. [70] C. Iwakura, H. Inoue, S. Nohara, *Encycl. Mater.: Sci. Technol.* 2001, 2001, 3923.
- [71] D. Mullangi, S. Nandi, S. Shalini, S. Sreedhala, C. P. Vinod, R. Vaidhyanathan, *Sci. Rep.* 2015, 5, 10876.
- [72] D. Mullangi, S. Shalini, S. Nandi, B. Choksi, R. Vaidhyanathan, *J. Mater. Chem. A* 2017, 5, 8376.
- [73] V. T. Le, H. Kim, A. Ghosh, J. Kim, J. Chang, Q. A. Vu, D. T. Pham, J. H. Lee, S. W. Kim, Y. H. Lee, *ACS Nano* 2013, 7, 5940.
- [74] X. Xu, J. Tang, H. Qian, S. Hou, Y. Bando, M. S. A. Hossain, L. Pan, Y. Yamauchi, *ACS Appl. Mater. Interfaces* 2017, 9, 38737.
- [75] K. Qi, R. Hou, S. Zaman, Y. Qiu, B. Y. Xia, H. Duan, *ACS Appl. Mater. Interfaces* 2018, 10, 18021.
- [76] Y. Huang, H. Hu, Y. Huang, M. Zhu, W. Meng, C. Liu, Z. Pei, C. Hao, Z. Wang, C. Zhi, *ACS Nano* 2015, 9, 4766.
- [77] R. Hou, M. Miao, Q. Wang, T. Yue, H. Liu, H. S. Park, K. Qi, B. Y. Xia, *Adv. Energy Mater.* 2020, 10, 1901892.
- [78] J. Li, X. Jing, Q. Li, S. Li, X. Gao, X. Feng, B. Wang, *Chem. Soc. Rev.* 2020, 49, 3565.
- [79] L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen, B. Wang, *J. Am. Chem. Soc.* 2015, 137, 4920.
- [80] S. Kandambeth, J. Jia, H. Wu, V. S. Kale, P. T. Parvatkar, J. Czaban-Jóźwiak, S. Zhou, X. Xu, Z. O. Ameer, E. Abou-Hamad, A.-H. Emwas, O. Shekhah, H. N. Alshareef, M. Eddaoudi, *Adv. Energy Mater.* 2020, 10, 2001673.

- [81] Y. Yusran, H. Li, X. Guan, D. Li, L. Tang, M. Xue, Z. Zhuang, Y. Yan, V. Valtchev, S. Qiu, Q. Fang, *Adv. Mater.* 2020, 32, 1907289.
- [82] L. Ascherl, T. Sick, J. T. Margra, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff, M. Döblinger, T. Clark, K. W. Chapman, F. Auras, T. Bein, *Nat. Chem.* 2016, 8, 310.
- [83] A. Ghoufi, K. Benhamed, L. Boukli-Hacene, G. Maurin, *ACS Cent. Sci.* 2017, 3, 394.
- [84] Y. Li, J. Chen, C. Zhao, *RSC Adv.* 2017, 7, 56676.

Made to Measure Squaramide COF Cathode for Zinc Dual-Ion Battery with Enriched Storage via Redox Electrolyte



3.1. Introduction:

Renewable energy has grown by 18% in the past decade. Efficient energy storage devices are required for harnessing intermittent renewable energy resources like wind, tide, or solar energy.^[1] Such storage devices need to suffice aqueous operation and environmental friendliness. Rechargeable zinc-ion batteries (ZIBs) display high theoretical capacity (820 mAh g⁻¹), high natural abundance, low redox potential (−0.76 V vs SHE), and most importantly, aqueous electrolyte compatibility, hence hitting the mark.^[2] Conventional ZIBs are usually assembled by coupling Zn anode with inorganic cathode materials such as MnO₂, V₂O₅, MoO₃, and ZnHCF,^[3–7] which are prone to hydrolyze/oxidize-reduce over time and carry intrinsic drawbacks like scarcity and toxicity. More crucially, the large hydration sphere of Zn(H₂O)_n²⁺ ions often suffer from sluggish kinetics or undesired phase/structural transformation during the intercalation/deintercalation into these oxides or ferrates reflected as poor rate-performance and cycling stability.^[8,9] Covalent organic frameworks (COFs) have recently garnered significant attention in energy storage applications.^[10–12] COFs are emerging porous crystalline polymeric materials with tailorable structures and functions. Their structure is characterized by π -stacked layers that generate uniform 1D channels lined with ion-interactive functionalities.^[13–16] The long-range ordered nano-channels and the subtle flexibilities of the organic framework facilitate the ultra-fast percolation of ions and form favorable electrode and electrolyte interfaces. Redox-active functional groups (e.g., —OH, —C=N—, —NH—, and C=O) comprising the polymers' backbone can coordinate Zn²⁺ ions in an electrochemical cell.^[17–20] However, chemically inert long carbon chains and benzene rings are null and void for Zn-ion energy storage. Previously, only a few COFs, such as HqTq-COF, PA-COF, and PI-COF, have been reported as electrode materials in aqueous ZIBs.^[21–25] Recently, Alshareef and co-workers engineered COF with and without a quinone-functional group to achieve a peak specific capacity of 344 mAh g⁻¹ at 0.1 A g⁻¹ for the latter.^[26] Meanwhile, Tao and co-workers reported another carbonyl-decorated COF with a storage capacity of 225 mAh g⁻¹ at 0.1 A g⁻¹, attributed to a synergistic co-insertion of Zn²⁺ and protons.^[27] Notably, in both cases, zinc sulphate was the electrolyte. We had earlier identified the eightfold drastic enhancement in capacitance brought out by the synergistic storage of H⁺ and polyiodide acting as a redox electrolyte.^[28] Iodide as a redox additive in other zinc-ion systems.^[29–32] Inspired by these findings, we wanted to explore if the iodide can perform similar mystic in a ZIB in an aqueous medium. Realizing, if successful, this could open doors for playing new redox games in many benign aqueous storage systems, which will

have a longer life than acidic ones. Here, we report a noble COF with squaric acid and phloroglucinol-based Zn dual ion battery. It consists of nitrogen and oxygen in such a fashion that it can chelate the cationic species during charging–discharging and boost the performance of the Zn-ion battery. For the first time, we combine a COF-electrode with redox-active ZnI₂ in a ZnSO₄(aq) electrolyte. Including iodide harvests, a remarkable threefold enhancement in capacity from 208 to 690 mAh g⁻¹ at 1.5 A g⁻¹, the highest among all the COF-derived ZIBs. To our best knowledge, such iodide-based redox active storage in a mildly acidic aqueous system is unreported. Importantly, our COF-derived ZIB can deliver the specific capacity over 6000 cycles without much fading and without any further addition of boosting iodide. Thus it is a truly employable chemistry. These observations open up crucial questions. What is the redox principle behind such a current surge? Why is the iodide redox chemistry in this aqueous electrolyte not a mere burst but a well-sustained reversible storage? This intricate reversible redox electrochemical storage is illustrated in this work (Scheme 1).

3.2. Results:

3.2.1. Synthesis and Characterizations of the Squaric Acid–Phloroglucinol Based COF (IISERP-COF22):

2,4,6-triformylphenol (24 mg, ~0.1 mmol) and the protected ligand 3,4-bis((4-((E)-benzylideneamino)phenyl)amino)cyclobut-3-ene-1,2-dione (70 mg, 0.15 mmol) were weighed into a Pyrex liner and was dissolved in ortho-dichlorobenzene (1 mL) and mesitylene (1.5 mL) and ethanol (2 mL) stirred for 20 minutes (Figure 3.1. and Table A.3.1., Appendix). To this mixture, 0.3 mL of glacial acetic acid was added. Then it was flash-frozen in a liquid nitrogen bath and sealed after 10 minutes. Contents were heated in an oven at 120 °C for 3 days and gradually cooled to room temperature over 12 hours. This yielded a red-brown colored solid, which was washed with DMA, dioxane, MeOH, acetone, and THF (85%, isolated yield). The final product was characterized by solid-state NMR analysis and IR. The bond formation of linkages for the synthesized COF was affirmed by solid-state NMR. The chemical shift (δ) at 180, 174, and 162 ppm (Figure 3.2.) also verifies the presence of C=O (from squaric acid), C=O (from keto-enol tautomerism), and =C–NH– bond, respectively. Fourier transform infrared spectroscopy. The COF material exhibits absorption peaks around 1788, 1646, and 1330 cm⁻¹ (Figure 3.3.), which can be assigned to the stretching vibrations of C=O (from squaric acid), C=O (from keto-enol tautomerism) and =C–NH– bonds.

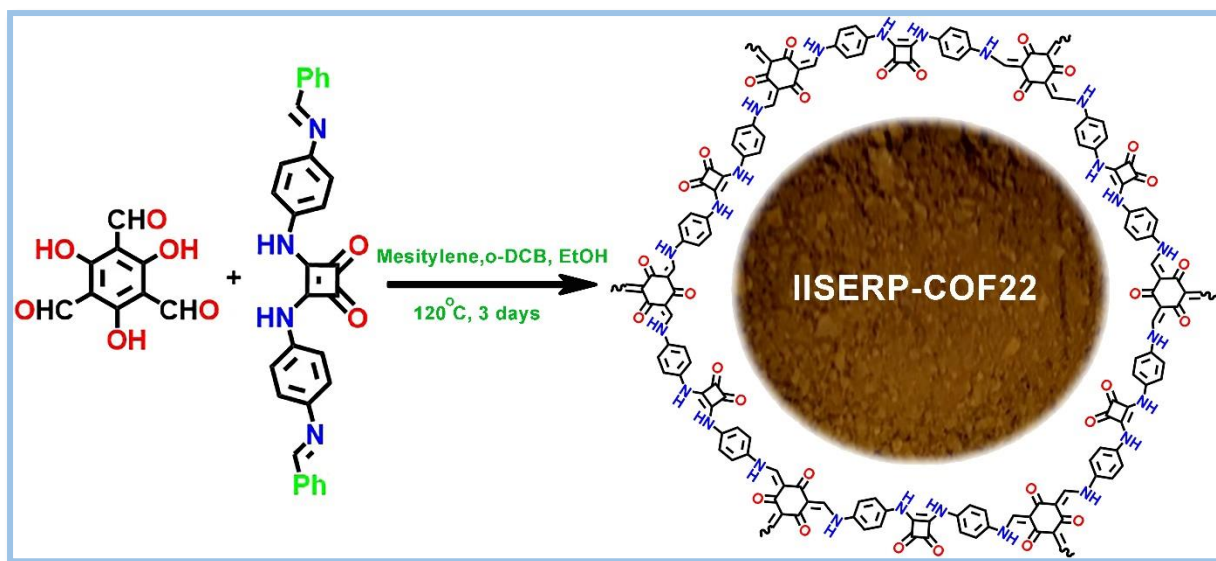


Figure 3.1. The synthesis of IISERP-COF22.

The absence of any absorption peak corresponding to terminal amine or aldehyde groups suggests the completion of the polycondensation reaction.

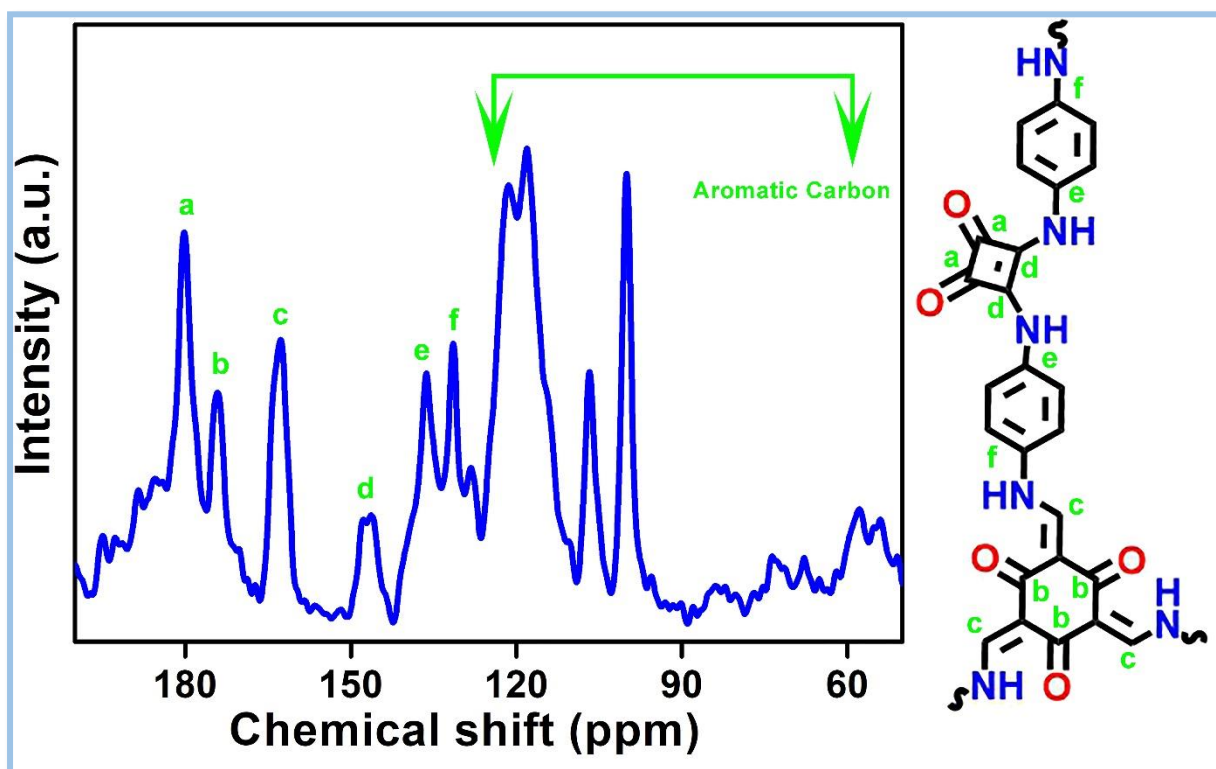


Figure 3.2. CP MAS ^{13}C -NMR spectra of the COF at 500 MHz a, b, c, d, e, and f are the positions of the corresponding peaks obtained from the NMR data.

It also surmises that the monomers retain their functional group integrity during polymerization. The majority of the COF exists in the β -ketoenamine with highly stabilized imine bonds.

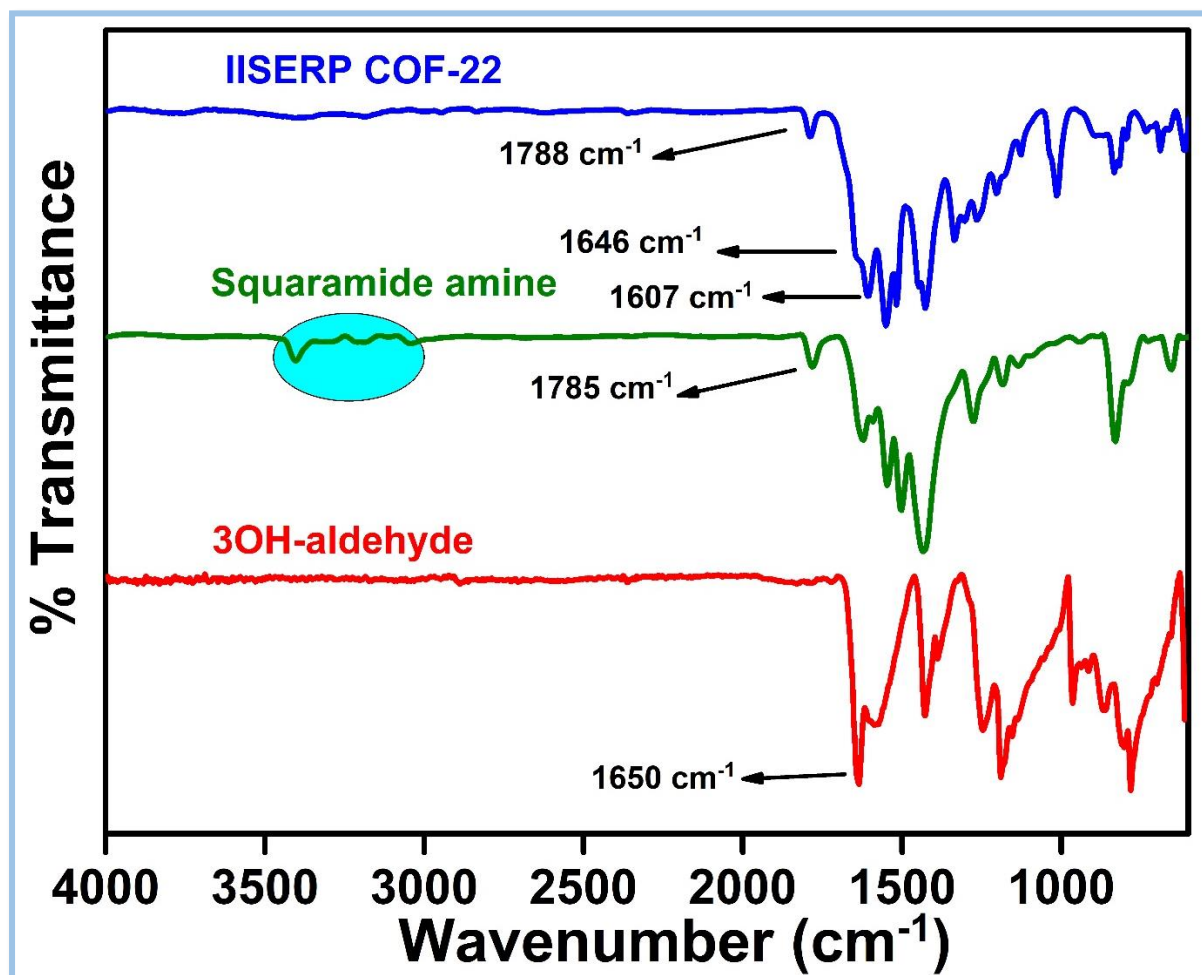


Figure 3.3. Comparison of the Fourier transform infrared (FT-IR) spectra of IISERP-COF22, squaramide amine, and triformyl phloroglucinol.

3.2.2 Structure modeling of IISERP-COF22:

To solve the structure of the COF, an initial structure was modeled via atomic-simulation using the Materials Studio V.8.0. The initial model was tried in P-6 as the highest possible space group; however, a satisfactory structure with acceptable bond lengths could not be obtained to match the experimental PXRD. Following this, symmetry had to be lowered to monoclinic and a satisfactory solution was obtained in the space group Pm.

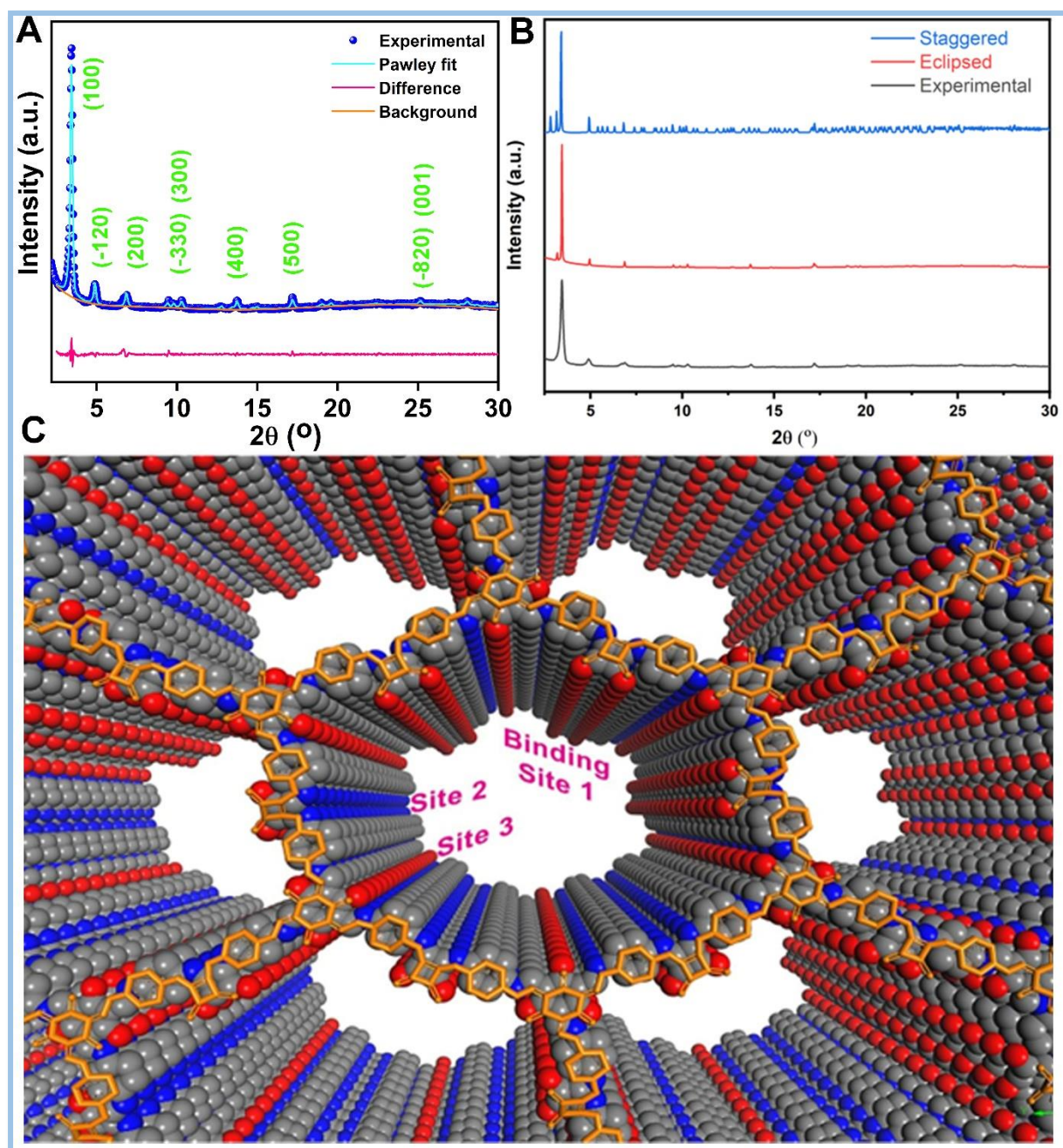


Figure 3.4. (A) A Pawley refinement of the eclipsed model against the experimental PXRD pattern. (B) A stack plot comparing the simulated PXRD's of the eclipsed and staggered models of IISERP-COF22 with the experimental pattern. (C) The polymeric structure of IISERP-COF22 shows the three different chelating binding sites present in them. Binding site 1: Squarate oxygens; Site 2: Amide nitrogens; Site 3: imine nitrogen + keto oxygen.

The structure could be solved as P-1 too. We have adopted Pm as the final structure given its higher symmetry. Both the eclipsed and staggered configurations were simulated. The eclipsed one had lower energy and matched the experimental PXRD much better (Figure 3.4.). Using this eclipsed model, we carried out Pawley refinement and the final lattice parameters and

profile parameters were extracted. The structure in Pm had the following parameters, Space group: Pm; $a = 36.104$, $b = 29.974$, $c = 3.5103$ Å; $\beta = 120.0$; $R_p = 3.98\%$; $R_{wp} = 5.44\%$. Formula sum: $C_{66} O_{12} N_{12}$; Formula weight 1152.8 g/mol. In the final modelled structure, the long squaramide linker results in a large pore of 30 Å (not factoring the vander Waal radii of atoms) in this eclipsed model (Figure 3.4. and Table A.3.2.), which agrees well with the experimental pore-size. An excellent Pawley fit was obtained with prominent h00 reflections and the 001 reflection, indicating high degree of crystallinity. Importantly, the 001 reflections occurring at $2\theta = 25.3^\circ$ matches well with the interlayer separation of 3.51 Å, suggestive of strong π - π stacking. This Pawley refined structure was used in all other calculations.

3.2.3 Characterization: Porosity and morphology

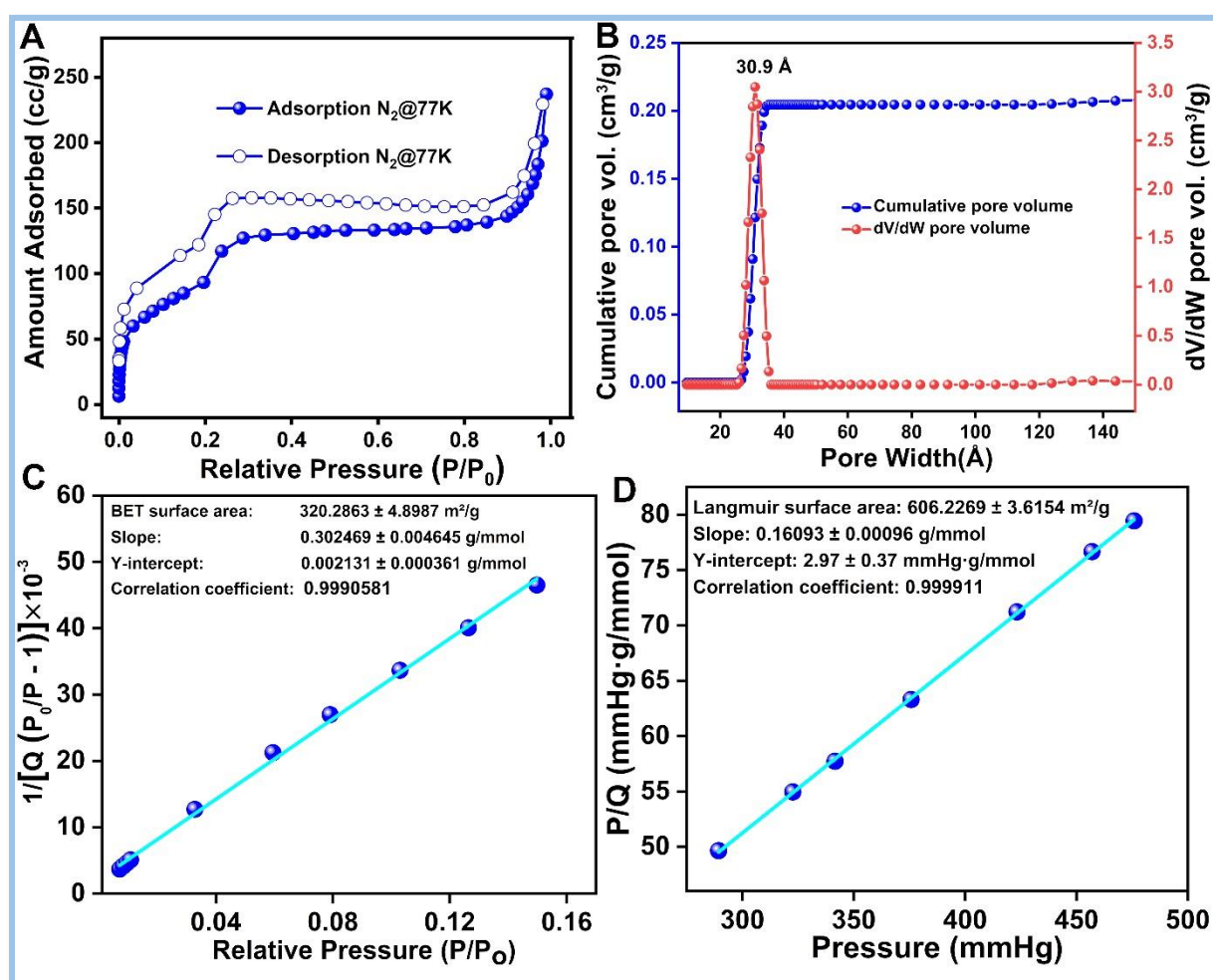


Figure 3.5. (A) N₂ adsorption-desorption isotherms of IISERP-COF25 at 77 K. Inset show a plot of the pore width vs. incremental pore volume of the COF. (B) A BET fit was obtained using the low-pressure region data of the N₂ adsorption isotherm. (C) The goodness-of-fit plot of the adsorption isotherm from the DFT model (Carbon at 77K). (D) A Langmuir fit was obtained using the N₂ adsorption isotherm.

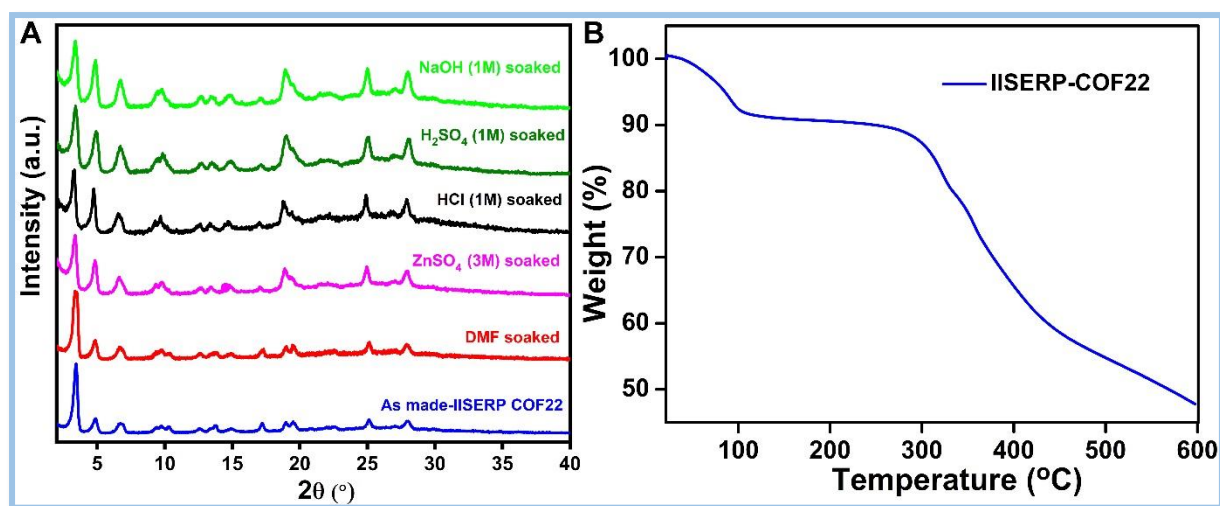


Figure 3.6. (A) Comparison of the PXRD patterns of the IISERP-COF22, soaked in acids, bases, and solvents displaying the COF's chemical stability. (B) Thermogravimetric analysis of the COF under N₂ flow at 5K/min rate.

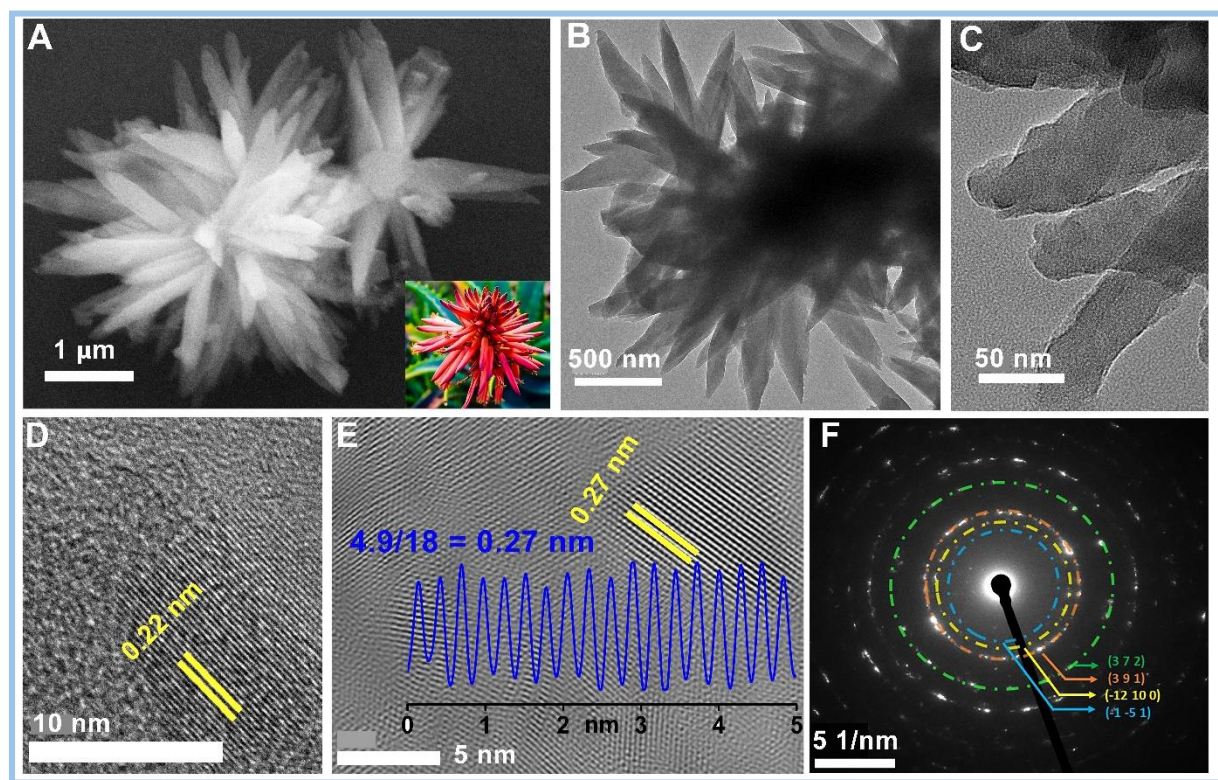


Figure 3.7. (A) FE-SEM images of IISERP-COF22. (B,C) HRTEM images of IISERP-COF22 at different resolutions. (D,E) HRTEM images at different resolutions with the assigned lattice fringes and inset showed a plot showing the average distances between the adjacent layers of the IISERP-COF22. (F) SAED patterns of the IISERP-COF22.

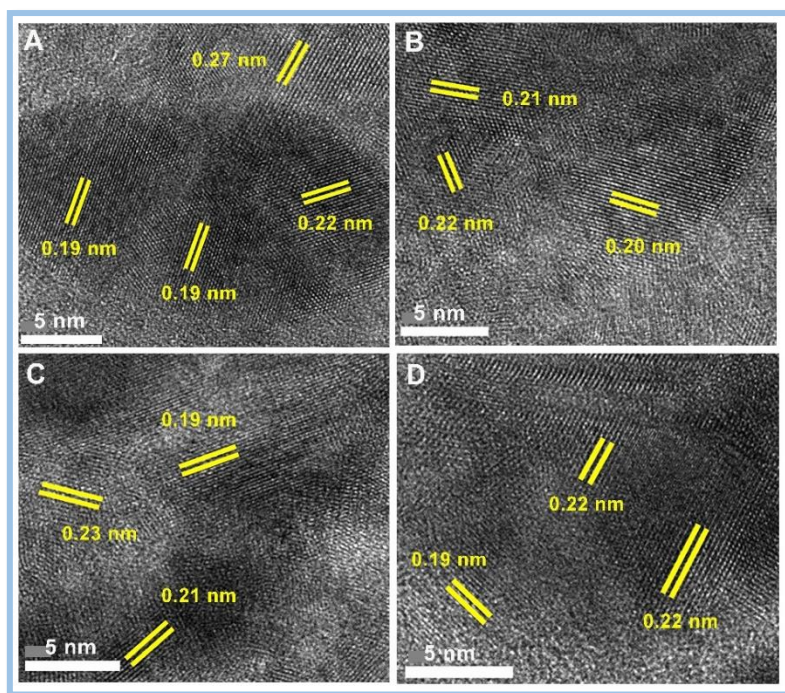


Figure 3.8. HRTEM images of the IISERP-COF22 lower resolution, the stacked layers giving rise to lattice fringes with different d-spacings.

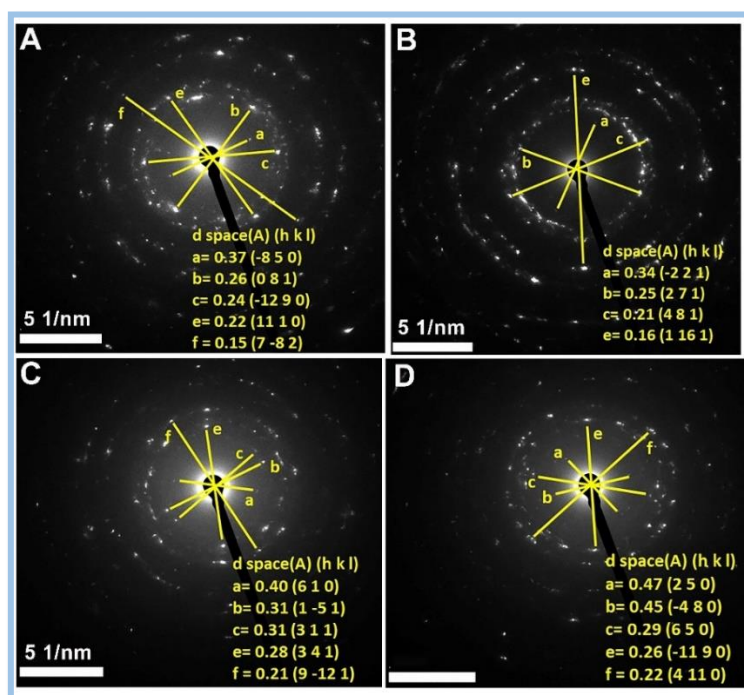


Figure 3.9. The SAED patterns of the as-synthesized IISERP-COF22 show the diffraction spots from different planes. The spots could be indexed to the hkl planes expected from the modeled structure. Some of them correspond to higher-order reflections.

The as-synthesized COF yielded a completely reversible type-IV nitrogen adsorption isotherm (Figure 3.5.A) characteristic of a mesoporous structure (Figure 3.5.B), with a Brauner–Emmet–Teller surface area of $320 \text{ m}^2\text{g}^{-1}$ and Langmuir surface area of $606 \text{ m}^2\text{g}^{-1}$ (Figure 3.5.C and 3.5.D). While the nonlocal density functional theory (NLDFT) fits to this, 77 K nitrogen adsorption isotherm confirmed the presence of uniform $30.9 \text{ \AA}$ sized pores. To check the chemical stability, the COF was soaked in HCl (1M), H_2SO_4 (1M), ZnSO_4 (3M), and NaOH (1M), respectively, and the PXRD patterns remain intact (Figure 3.6.A). Further, thermogravimetric analysis shows the thermal stability of the COF (stable up to $\approx 280^\circ\text{C}$) (Figure 3.6.B). The COF shows a dendritic fibrous morphology under field-emission scanning electron microscopy (FE-SEM) (Figure 3.7.A and Figure A.3.2.), well-suited for aqueous electrolyte wetting, which agrees with the solvent loss observed in the TGA. Furthermore, high-resolution transmission electron microscopy (HRTEM) reveals that the aggregated fibers originated from stacking thick multi-layers garnished by fine micron-sized pores along the surface (Figures 3.7. B-C and Figure A.3.3.). At higher resolution, the lattice fringes of the IISERP-COF22 can be seen, and the selected area electron diffraction (SAED) displays well-defined diffraction spots, which index extremely well to the d-spacings derived from the powder pattern of the COF (Figures 3.7.D–F, 3.8. and 3.9.).

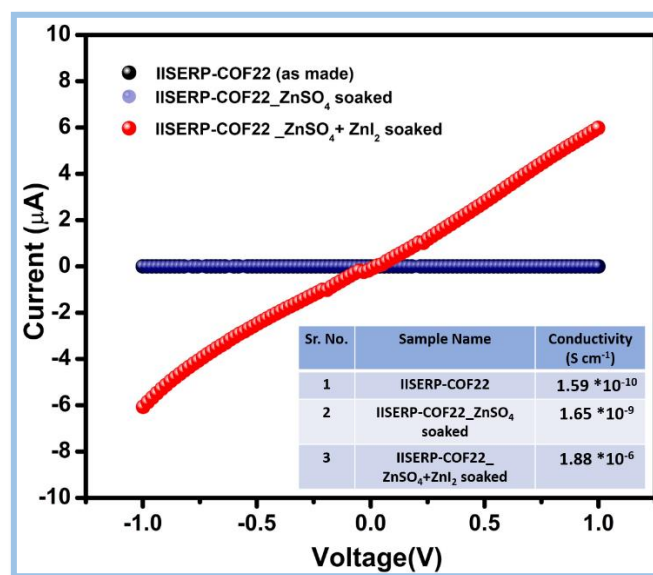


Figure 3.10. Comparative I–V plots of the as-made COF, COF soaked in ZnSO_4 , and the COF soaked in 3M $\text{ZnSO}_4 + 0.2\text{M ZnI}_2$ obtained on a two-probe conductivity set-up using Keithley2450 source meter. Conductivity at room temperature: IISERP-COF22 = $1.59 \times 10^{-10} \text{ S cm}^{-1}$; IISERP-COF22 in soaked in 3M ZnSO_4 = $1.65 \times 10^{-9} \text{ S cm}^{-1}$; IISERP-COF22 in soaked in 3M $\text{ZnSO}_4 + 0.2\text{M ZnI}_2$ = $1.88 \times 10^{-6} \text{ S cm}^{-1}$.

To understand the electronic conductivity, we performed the two probe bulk conductivity measurements on pressed pellets of the as-made COF, and the COF soaked overnight in 3M $\text{ZnSO}_4(\text{aq})$ and 3M $\text{ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$ solutions, respectively. We observe a ≈ 1000 -fold enhancement in electronic conductivity as we go from neat $\text{ZnSO}_4(\text{aq})$ to the $\text{ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$ (Figure 3.10.).

3.2.4 Electrochemical Measurements in a Three-Electrode Mode

The Zn^{2+} storage behavior of the COF electrode was assessed in a conventional three-electrode system with an Ag/AgCl as a reference electrode, $1 \times 1 \text{ cm}^2$ Toray paper as a working electrode, graphite rod as a counter electrode, and 3M $\text{ZnSO}_4(\text{aq})$ as an aqueous electrolyte. The electrochemical reversibility of COF was estimated by cyclic voltammetry (CV). As the CV profiles show (Figure 3.11.A), there are two reduction peaks (0.26 and 0.5V) and two oxidation peaks (0.37 and 0.51V), which correspond to two redox states of the COF during the cation insertion/de-insertion process. We employed a redox electrolyte system to improve the charge storage capacity of the Zn-ion battery so that it qualifies for practical usage. Upon the addition of 0.2M solution of ZnI_2 to 3M $\text{ZnSO}_4(\text{aq})$, a notable enhancement in the current of CV was observed (Figures 3.11.A and 3.11.B). To understand the mechanism of charge storage in the composite electrode from the CV, a plot of the log of anodic peak current versus the log of scan rate yields a ‘b’ value of 0.63 for neat 3 m ZnSO_4 , and upon addition of ZnI_2 , the b value obtained is 0.52, which indicates the redox-activity in both electrolyte systems (Figures A.3.6. and A.3.7.). We prefer ZnI_2 as a redox additive due to its exceptionally low toxicity, non-hazardous, and mainly for its ability to generate a range of redox-active species. Under the redox potential, ZnI_2 can generate poly-iodide ions (I_n^-) with different redox pairs of iodide on the surface of the electrode, such as $3\text{I}^-/\text{I}_3^-$, $\text{I}_2/2\text{IO}_3^-$, $2\text{I}^-/\text{I}_2$, and $2\text{I}_3^-/3\text{I}_2$.^[30–32,36] Here, we report for the first time the use of a redox-active additive (ZnI_2) with $\text{ZnSO}_4(\text{aq})$ as the electrolyte for COF-based Zn-ion charge storage. Perceptible changes occur in their CV curves. The $\text{ZnI}_2 + \text{ZnSO}_4(\text{aq})$ system covers an extra-large area compared to neat $\text{ZnSO}_4(\text{aq})$ (Figures 3.11.A and 3.11.B). A substantial enhancement in the overall current was observed from the CV. Strikingly, the high activity of iodides in sulfuric acid and other acidic media is an established chemistry.^[37] However, the increased activity of ZnI_2 in an aqueous zinc sulphate solution is noteworthy.^[30,38] This is, in fact, due to the exceptionally high solubility of ZnI_2 compared to even KI (ZnI_2 solubility is 450/100 g of water (20°C) versus KI solubility is 150/100 g of water at 20°C; both are constituted by ionic bonds). Further, we performed control experiments to

investigate the role of each component in gaining large capacity in the redox electrolyte system using cyclic voltammetry (Figures A.3.8.- A.3.10.).

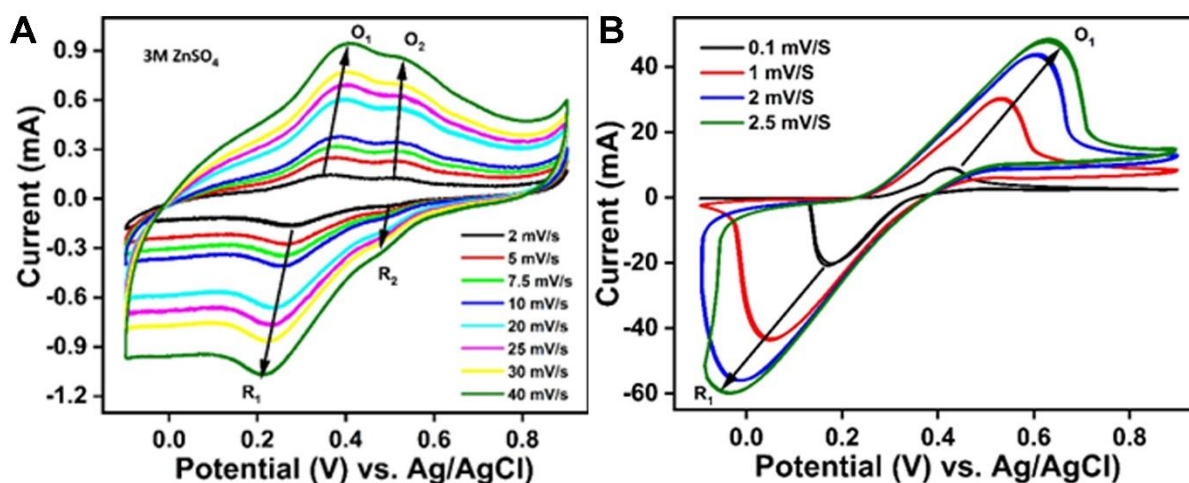


Figure 3.11. (A) All CVs shown in this figure have been measured in a three-electrode assembly. The plots of the composite were measured using 3M ZnSO₄ as electrolyte at different scan. (B) The plots of the composite were measured using 3M ZnSO₄+ 0.2M ZnI₂ as electrolyte at different scan. Note for A: In the case of 3M ZnSO₄(aq) electrolyte system, there are two reduction peaks (R₁=0.27, and R₂= 0.49 V vs. Ag/AgCl @2mV/s), which correspond to reduction states of the COF during the cation (Zn²⁺ ions) insertion processes. There are two oxidation peaks (O₁= 0.36, and O₂= 0.51 V vs. Ag/AgCl @2mV/s), which correspond to oxidation states of the COF during the cation (Zn²⁺ ions) de-insertion process. Moreover, all the reduction and oxidation peak currents increase with the increase of scan rate. There is a shift in the peak positions of reduction and oxidation observed upon the increase in scan rate. Note for B: in the case of 3M ZnSO₄ + 0.2M ZnI₂(aq) electrolyte system, the current intensity jumps up, and predominately one oxidation peak (O₁=0.43 V vs. Ag/AgCl @0.1 mV/s), which correspond to oxidation of I⁻ to I₂ on the surface COF, an associated redox action will be occurring at the COF too. In a concerted fashion, this I₂ on the COF surface will combine with the I⁻ available from the electrolyte and form I₃⁻, whose presence is confirmed by XPS analysis. In the reduction cycle, a reduction peak is observed (R₁= 0.16 V vs. Ag/AgCl @2mV/s), which corresponds to a reduction of I₃⁻ or I₂ to I⁻ on the surface COF. Moreover, all the reduction peak currents and oxidation peak reduction peak currents increase with the increase of scan rate. There is a shift in the peak positions of reduction and oxidation observed upon the increase in scan rate. Importantly, compared to the ZnSO₄ case, in the ZnI₂ case, the current is so high which suggests the redox storage of the polyiodide happens in substantially larger amounts compared to just Zn²⁺. Thus, the polyiodide's storage occurs synergistically with the storage of Zn²⁺ ions to enhance the overall capacity.

We also performed the CV measurements with other redox-active electrolytes like 3M ZnSO₄+0.2M AlI₃, 3M ZnSO₄ + 0.2M KI, and 3M ZnSO₄ + 0.2M ZnI₂. Among all, 3M ZnSO₄

+ 0.2M ZnI₂ gave the highest current response suggesting it can store more charge compared to other redox-electrolyte systems (Figure A.3.10.).

3.2.5. Electrochemical Performance of COF through Coin Cell Configurations

To explore the unique functional group advantage of the COF for Zn-ion energy storage, the electrochemical performance of COF as cathode was tested via assembling a two-electrode zinc ion battery in the presence of commercial Zn foil anode and 3M ZnSO₄(aq) aqueous electrolyte (Figure 3.12. A). The excellent improvement of current in the cyclic voltammogram of the COF in the redox electrolyte encouraged us to carry out realistic measurements of two-electrode coin cells with the configuration of Zn//COF with plausible interaction among various chelating sites available in the COF's skeleton and Zn-ion (Figures 3.12. A,B). The coin cell was fabricated by coating the active material, a slurry made using 80% COF dispersion in ethanol, 15% of Super P carbon, and 5% of Nafion binder on a carbon cloth and cellulose paper as a separator. Variable scan rate CV measurements were conducted in the range of 0.2–1.6 V using these coin cells with ZnSO₄(aq) and ZnSO₄+ZnI₂(aq) electrolyte, respectively (Figure 3.12.C; Figures A.3.11. and A.3.12. Appendix). Archetypical rectangular-shaped CVs were observed with prominent redox peaks at variable scan rates in the case of the 3 m ZnSO₄(aq) electrolyte. The cyclic voltammetry (CV) profiles (Figure 3.12.C and Figure A.3.11) were obtained at the scan rate of 0.1 mV s⁻¹ of COF-based Zn//COF coin cells. There are two reduction peaks (0.89 and 1.27 V) versus Zn²⁺/Zn and two oxidation peaks (1.04 and 1.19V) versus Zn²⁺/Zn with 3M ZnSO₄(aq) electrolyte, which corresponds to two redox states of the COF due to the presence of carbonyl amine and imine functional groups. The robust imine-and amide bonds holding the COF framework permit use of such concentrated Zn²⁺ solutions (Figure 3.12.B and Scheme 3.1). However, a reduction peak at 1.10 V versus Zn²⁺/Zn and an oxidation peak at 1.57 V versus Zn²⁺/Zn were observed in the redox electrolyte system (Figure 3.12.C). The current gain has been enhanced at the higher CV scan rates in both the electrolyte system. A remarkable enhancement in the overall current was observed from the CV in the redox electrolyte system (Figure 3.12.C). The galvanostatic charge–discharge (GCD) profile of the Zn//COF coin cells exhibits its charge-storage properties in the adopted potential window with a voltage plateau in both electrolyte systems. Herein, the GCD analysis shows that the IISERP-COF22 cathode presents a significantly high discharge capacity of 208 mAh g⁻¹ at the current density of 1.5 A g⁻¹ in the 3M ZnSO₄(aq) electrolyte (Figure 3.12.D). The significantly superior dis-charge capacity of 690 mAh g⁻¹ at the current density of 1.5 Ag⁻¹

(theoretical 820 mAh g^{-1}) was observed from the GCD measurements in the $3\text{M ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$ electrolyte, which is among the best-performing COF based ZIBs (Figure 3.12.E and Table 3.1.). The discharge of iodide into the medium is quite aggressive (current builds up

Table 3.1. Comparison of the specific capacity of the best COF and MOF derived Zn ion battery.

Electrode	Electrolyte	Voltage (V)	Capacity (mAh g^{-1})/ Current density (A g^{-1})	References
PA-COF//Zn	1 M ZnSO_4	0.2-1.8	170/1	<i>ACS Energy Lett.</i> 2020 , 5, 2256–2264
AC//Zn	2 M ZnSO_4	0.2-1.8	121/0.1	<i>Energy Storage Mater.</i> 2018 , 13, 96-102
HCS//Zn	2 M ZnSO_4	0.15-1.95	65.1/0.1	<i>J. Mater. Chem. A</i> 2019 , 7, 7784-7790
Poly(4,4'TD) modified AC//Zn	2 M ZnSO_4	0.1-1.9	188/0.3	<i>J. Mater. Chem. A</i> 2019 , 7, 23076-23083.
PSC-A//Zn	1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	0.2-1.8	184/0.2	<i>Adv Mater</i> 2019 , e1904948
MCHS//Zn	2M ZnSO_4	0.2-1.8	174.7/0.1	<i>Energy Storage Mater.</i> 2020 , 28, 307-314
$\text{Cu}_3(\text{HHTP})_2//\text{Zn}$	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	0.5-1.3	228/0.05	<i>Energy Storage Mater.</i> 2020 , 25, 858-865
HNPC//Zn	1 M ZnSO_4	0-1.8	177.8/4.2	<i>Chem. Sci.</i> 2019 , 10, 8889.
HqTq COF//Zn	3 M ZnSO_4	0.2-1.8	276/0.125	<i>Nat. Commun.</i> 2019 , 10, 4948
BT-PTO COF//Zn	3 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$	0.4-1.5	213/1	<i>Angew. Chem.Int. Ed.</i> 2022 , 61, e2021175
Tp-PTO-COF//Zn	2 M ZnSO_4	0.4–1.5	250.1/1	<i>Chem. Sci.</i> , 2022 , 13, 2385
IISERP-COF22//Zn	3 M ZnSO_4 3 M $\text{ZnSO}_4 + 0.2 \text{ M ZnI}_2$	0.2-1.6	208/1.5 690/1.5	(This work)

rapidly). It is worth mentioning the ability of this imine–amide COF to sustain these conditions. We verified this also by adding the same concentration of KI as the iodide source, which yielded current enhancement but was lower than ZnI_2 , which suggests the Zn^{2+} being the common ion between the sulphate and the iodide is also important (Figures A.3.10.).

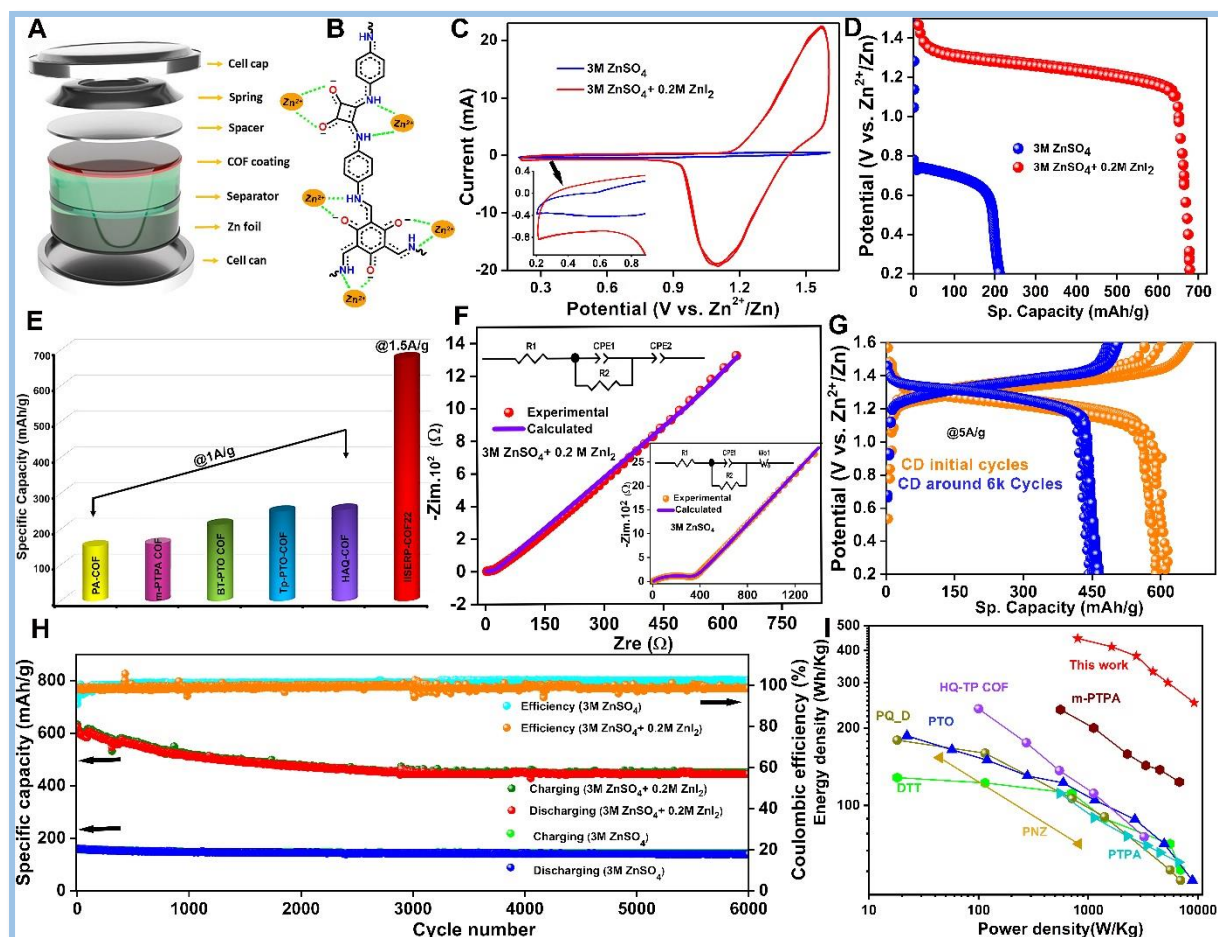


Figure 3.12. (A) Diagrammatic representation of the fabrication of lab scale aqueous Zn//COF coin cell. (B) The probable interactions showing the Zinc insertion with the functional sites of IISERP-COF22 under the applied potential. (C) Comparative CV plots of the COF-based coin cells were measured using $3\text{M ZnSO}_4(\text{aq})$ and $3\text{M ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$ as an electrolyte at 5 mV s^{-1} . (D) Comparative galvanostatic charge–discharge curves of the COF based coin cells were measured using $3\text{M ZnSO}_4(\text{aq})$ and $3\text{M ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$ as an electrolyte at 1.5 A g^{-1} . (E) An up-to-date comparison of the specific capacity of some high-performing COF-based ZIBs. (F) The impedance analysis of the coin cell fabricated using $3\text{M ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$ and the inset shows the impedance analysis of the coin cell fabricated using $3\text{M ZnSO}_4(\text{aq})$. (G) Comparative galvanostatic charge–discharge curves of the COF-based coin cells were measured using $3\text{M ZnSO}_4 + 0.2\text{ m ZnI}_2(\text{aq})$ as an electrolyte at 5 A g^{-1} . (H) Cyclic stability over 6000 cycles of COF-based coin cell was measured using $3\text{M ZnSO}_4(\text{aq})$ and $3\text{M ZnSO}_4 + 0.2\text{ m ZnI}_2(\text{aq})$ as an electrolyte at 5 A g^{-1} . (I) A Ragone plot displayed

the overall performance of IISERP-COF22 ZIB with respect to other leading metal-free COF and polymer-based ones. All CVs shown in this figure have been measured in a three-electrode assembly.

This is likely because they find well-fitting homogeneous binding sites dissimilar to K^+ . The impedance spectroscopy measurements of coin cells reveal a significant lowering of resistance upon switching the electrolyte from $ZnSO_4(aq)$ to $ZnSO_4 + ZnI_2(aq)$ (Figure 3.12.F). Upon the inclusion of ZnI_2 in the electrolyte, both resistances, ohmic (R_1) and charge transfer resistance (R_2), decrease. Thus, the ZnI_2 , as an active redox additive, plays a crucial role in lowering the overall resistance. In addition, the participation of the polyiodide species generated from electrolytes reduces the electrode–electrolyte interface resistance. The equivalent circuit was employed for fitting the Nyquist curve obtained from $ZnSO_4(aq)$ as well as $3M ZnSO_4 + 0.2M ZnI_2(aq)$ electrolytes using the ZView software (Figure 3.12.F). The R_1 represents the contribution of the electrolyte's ionic resistance and the intrinsic electronic resistance of the electrode material. The ohmic (R_1) decreases from 4.7 to 1.2Ω upon switching the electrolytes from $ZnSO_4(aq)$ to $3M ZnSO_4 + 0.2M ZnI_2(aq)$. However, a drastic decrease in the charge transfer resistance R_2 was observed from 325.6 to 21.1Ω upon switching the electrolytes from $ZnSO_4(aq)$ to $3M ZnSO_4 + 0.2M ZnI_2(aq)$, which is positioned parallel to the constant phase element 1 (CPE_1), represents the redox reactions at the electrode–electrolyte interface. CPE_2 , which accounts for the mass capacitance in the low-frequency regime. The fits yielded low χ^2 values and $>2.5\%$ error. The observed resistance R_1 , R_2 , CPE_1 , and CPE_2 are all in the acceptable range.

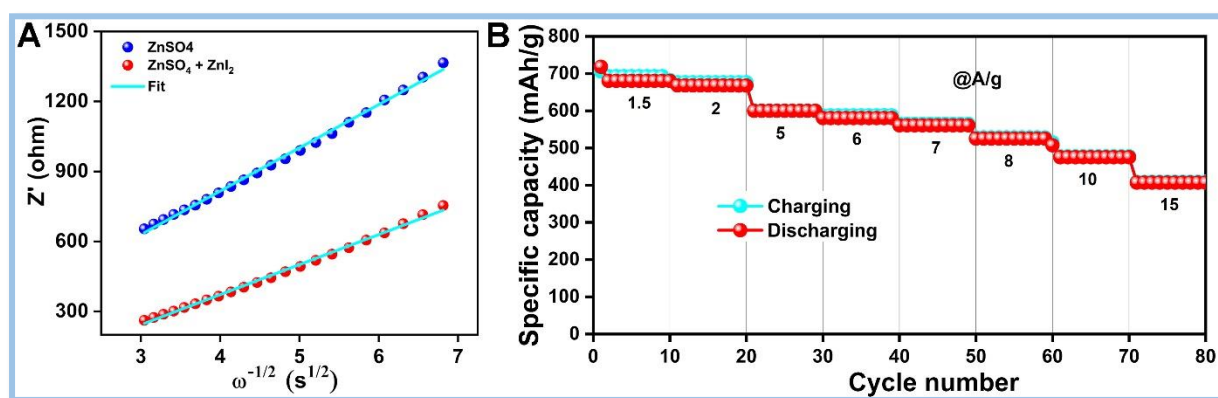


Figure 3.13. (A) A plot of the Z_{Re} vs. Inverse square root of frequency (ω) of COF in $3M ZnSO_4$ (slope 185.5) and $3M ZnSO_4 + 0.2M ZnI_2$ (slope 128.8) electrolyte the slope of the linear fit reflects the diffusion kinetics. (B) Cyclic performance of $Zn//COF$ coin cell, fabricated using $3M ZnSO_4 + 0.2M ZnI_2$ as an electrolyte in the current range of $1.5 - 15 A/g$.

We calculated the diffusion coefficients inside the COF using the Z' versus $\omega^{-1/2}$ plot.^[39,40] The low-frequency spectrum of the impedance plot yielded the characteristic linear fits (Figure 3.13.A and Table 3.2.), from which the diffusion coefficients were estimated to be $7.67 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the Zn^{2+} ions and $1.40 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the I_3^- with 3M $\text{ZnSO}_4(\text{aq})$ and 3m $\text{ZnSO}_4 + 0.2\text{M ZnI}_2(\text{aq})$, respectively

Calculation of Zinc ion diffusion co-efficient in ZnSO_4 and $\text{ZnSO}_4+\text{ZnI}_2$ electrolyte:

$$D = \left[\frac{RT}{\sqrt{2}AF^2\sigma_w C} \right]^2$$

Where,

D- diffusion coefficient of ions, $\text{m}^2 \text{ s}^{-1}$ using σ_w

A - area of electrode, m^2

σ_w -Warburg coefficient, $\Omega \text{ m}^2 \text{ s}^{-1/2}$

C - concentration of Zn ions in mol m^{-3}

R - gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

T - temperature, K

F - Faraday constant = 96485 C mol^{-1}

Table 3.2. List of Zinc ion diffusion coefficients in ZnSO_4 and $\text{ZnSO}_4+\text{ZnI}_2$ electrolyte

Electrolyte	Warburg coefficient (σ) $\Omega \text{ m}^2 \text{ s}^{-1/2}$	Diffusion coefficient ($D_{\text{Zn}^{2+}}$) m^2/s	Diffusion coefficient ($D_{\text{Zn}^{2+}}$) cm^2/s
$\text{ZnSO}_4(\text{aq.})$	0.024	7.67512E-10	7.67512E-6
$\text{ZnSO}_4+\text{ZnI}_2(\text{aq.})$	0.016	1.40907E-9	1.40907E-5

Notably, the magnitude of the ionic conductivity is much higher for the redox electrolyte system than the electronic one (10^{-3} vs 10^{-6} Scm^{-1}). To evaluate the cell's performance in a more practical and demanding variable current densities from 1.5 to 15 A g^{-1} , we carried out GCD measurements that yield retention of high specific capacities even at higher current densities, representative of faster charging–discharging (Figure 3.13.B). Remarkably, a charge–discharge curve with a smooth plateau at 1.3 V with very limited dropout voltage and super-flat platform (Figure 3.12.G), something that is observed for the high-voltage cathodes like the cyano ferrates.^[41] Importantly, this super-flat platform is maintained to a very high specific capacity of 600 mAh g^{-1} at 5 A g^{-1} ($\approx 23 \text{ C}$), substantially higher than what is observed for the cyano ferrates supported on conducting carbon (67 mAh g^{-1} at 2.5 C).^[41] We are reporting for the first time such stable charge–discharge performance at such high current densities with such large specific capacities for a COF-derived ZIB cathode.^[21–28] We attribute this to the high degree of crystallinity leading to the uniform exposure of the well-defined chelating squarate units for the favorable binding with the guest ions. A comparison with some

of the top-performing ZIB cathodes shows that this high specific capacity at this discharge voltage plateau (1.3 V) is record-breaking (Table 3.3).^[25,27,41–44] This instills new promises from COFs. This large capacity (450 mAh g⁻¹ at 5 A g⁻¹) is retained after 6000 cycles (Figure 3.12.H).

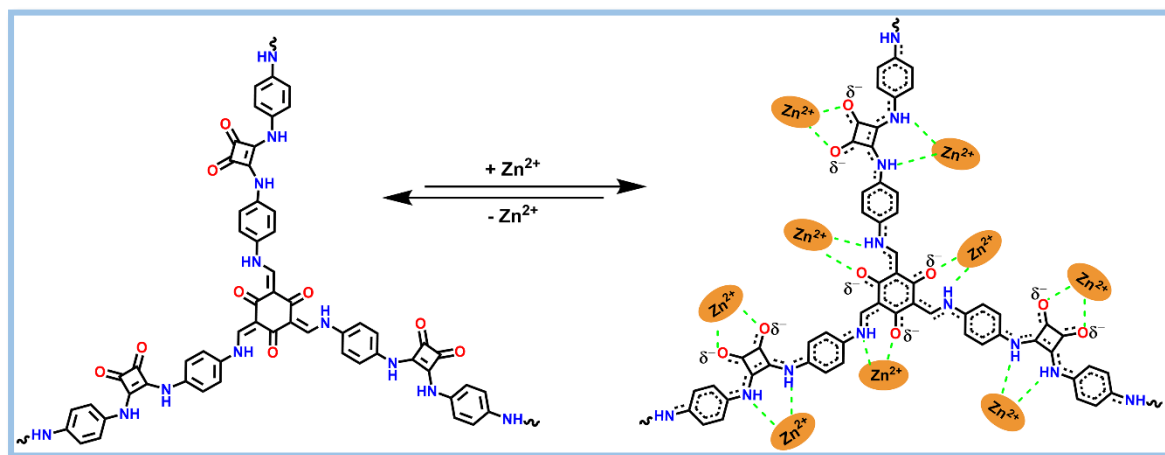
Table 3.3. Comparison of the specific capacity and charge-discharge Super Flat platform values of top-performing aqueous ZIB cathodes.

Electrode	Electrolyte	Discharge Plateau Voltage (V)	Capacity (mAh g ⁻¹)/ Current density (A g ⁻¹)	References
ZnHCF//Zn	1M Zn(CF ₃ SO ₃) ₂	1.7	50/1	<i>Nano-Micro Lett.</i> 2020, 12, 75
VS ₂ //Zn	1M ZnSO ₄	0.6	121.5/1	<i>Adv. Energy Mater.</i> 2017, 7, 1601920
Iodine/N-doped-carbon (I ₂ /N-C)	1 M ZnSO ₄	1.2	150/1.4	<i>Adv. Mater.</i> 2020, 32, 2000287
Zn _x MnO ₂ ·H ₂ O//Zn	1M ZnSO ₄ + 0.1M MnSO ₄	1.2	175/1	<i>RSC Adv.</i> , 2018, 8, 15703-15708
Bi ₂ O ₃ //Zn	6M KOH + 0.3M Zn(Ac) ₂	0.7	200/1	<i>Nano Energy</i> 2020, 71, 104583
BT-PTO COF//Zn	3 M Zn(CF ₃ SO ₃) ₂	0.8	213/1	<i>Angew. Chem.Int. Ed.</i> 2022, 61, e2021175
Tp-PTO-COF//Zn	2 M ZnSO ₄	0.8	250.1/1	<i>Chem. Sci.</i> , 2022, 13, 2385
IISERP-COF22//Zn	3 M ZnSO ₄ + 0.2 M ZnI ₂	1.3	690/1.5	(This work)

No visible cracks or large dendritic island is seen even after this many cycles (Figure A.3.13.); it looks comparable to some of the other stable aqueous ZIBs based on inorganic electrodes.^[45,46] The post-cyclic characterization elemental mapping and EDAX analysis was also carried out for both electrolyte systems (Figures A.3.14.– A.3.17.). Figure 3.12.I displays a Ragone plot expressing the overall performance of the IISERP-COF22 ZIB with respect to other leading metal-free COF and polymer-based ones. Our COF cathode, coupled with redox electrolyte, brings out the true potential of ZIB.^[18,21,47–51] Further, we performed control experiments with the Zn//COF coin cell fabricated using only 0.2 m ZnI₂(aq). Due to insufficient ions, high charge transfer resistance in the case of 0.2M ZnI₂ (800Ω) was obtained in the impedance analysis. It is even much higher than the charge transfer resistance observed in the case of 3M ZnSO₄ (325Ω) and 3M ZnSO₄ + 0.2M ZnI₂ (21Ω). The specific capacity

obtained 28 mAh g^{-1} at 0.1 A g^{-1} in GCD measurement was much lower than the specific capacity compared to 3M ZnSO_4 (208 mAh g^{-1} at 1.5 A g^{-1}) and $3\text{M ZnSO}_4 + 0.2\text{M ZnI}_2$ (690 mAh g^{-1} at 1.5 A g^{-1}) (Figure A.3.18.).

3.2.6 Dual-Ion Charge-Storage Mechanism of the COF

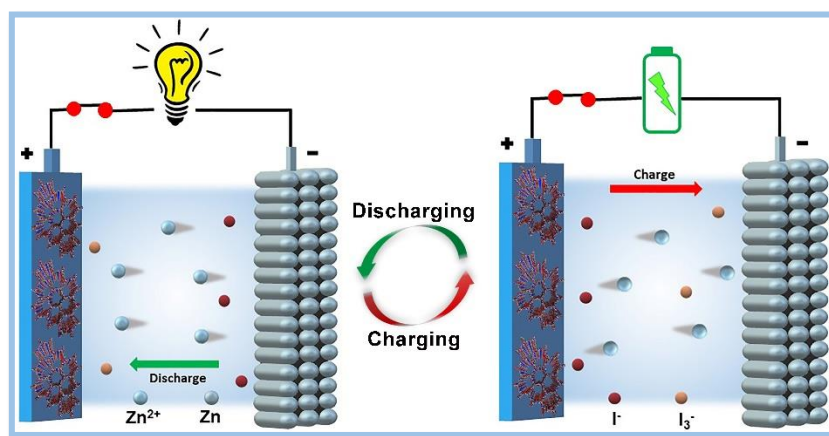


Scheme 3.1. The possible mechanism of the interaction of COF with Zn^{2+} ions during the discharge/charge process in the electrochemical reaction.

In the first case with ZnSO_4 (3M) only, Due to its high surface area and a high degree of crystallinity, it contains long-range ordered nano-channels, and the subtle flexibilities of the organic framework facilitate the ultra-fast percolation of ions and form favorable electrode and electrolyte interactions. Redox-active functional groups like $=\text{C}-\text{NH}-$, $-\text{NH}-$, and $\text{C}=\text{O}$ (from squaric acid), $\text{C}=\text{O}$ (from keto-enol tautomerism) decorated on the polymer backbone are capable of chelating/de-chelating Zn^{2+} ions reversibly during the electrochemical process, which is reflected in the higher specific capacity of the Zn-ion battery (Scheme 3.1.). This explains the high performance observed in 3M ZnSO_4 electrolytes. Also, the COFs are very stable in adverse chemical environments and insoluble in electrolyte solutions, which helps them withstand multiple charge-discharge cycles.

The charge storage mechanism of our COF-based zinc ion battery can be explained like this. Initially, all iodide ions present near the surface of the working electrode are converted to I_2 through the electrochemical oxidation process or direct oxidation with the aqueous medium ($2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^-$ $E_0 = -0.54 \text{ V}$ [Equation (1)] implies favorable), then I_2 interacts with coated material on the working electrode and bulk electrolyte (Scheme 3.2.). However, only the ability of the I_2 to increase the electronic conductivity of COF has been explained so far; its advantage in a true charge-storage system has not been exploited.^[52–54] Here, in this ZIB system, we

realize the true potential of the increased electronic and ionic conductivity, and we can explain exactly the chemistry involved at the anode and the cathode.



Scheme 3.2. The possible mechanism during the Charging–discharging process of Zn-ion battery. IISERP-COF22 is used as the cathode, Zn metal as the anode, and aqueous Zn metal salt as the electrolyte.

3.2.6.1. Discharge

While Zn oxidizes to Zn^{2+} and binds to the chelating sites, it brings two electrons to the system, simultaneously, the iodide ions introduced by the ZnI_2 get attracted to the surface of the positively biased anode. However, unlike SO_4^{2-} , which already resides in the highest oxidized form, the iodide is electrochemically favorable for anodic oxidation. This introduces additional $2e^-$, thus further boosting the current (see Equation (1)). Thus, it generates iodine into the medium. Now, this iodine reacts with the free I^- to form I_3^- . Thus, I_2 , I^- , and I_3^- become the most favorable species residing in the electrolyte or on the electrode surface at this point, as confirmed by spectro-electrochemistry later in the text. This completes the discharge (Scheme 3.2.). Thus both Zn^{2+} and polyiodides contribute crucially to the overall charge storage making the system a dual-ion battery.

3.2.6.2. Charge

During charging, the COF gets biased as positive, and the zinc metal is biased as negative. The Zn^{2+} ions get repelled at the positively charged COF; hence travel back to the zinc anode through the electrolyte. Now, how positive the COF gets, and how quickly it depends on its conductivity, and this will set up the necessary driving force to push the Zn^{2+} ions away from

the COF. As mentioned earlier and as observed from the literature,^[52–54] the iodine adsorbed on COF naturally increases its electronic activity and can alter the frontier orbitals in favor of accepting electrons,^[55] which means the COF charged with iodine will now interact better with the current collector in accepting the electrons from the external circuit—rapidly and in large amounts. IISERP-COF22, with its highly polarizable groups, can adsorb this iodine/iodide through strong coulombic interactions,^[54] increasing their electronic conductivity and can accumulate electrons from the external circuit to become strongly negative. This negatively biased COF surface repels the Zn^{2+} ions setting up a driving force; this explains the high energy density and the power density. We acknowledge that the process of having to solvate and desolvate when the Zn^{2+} combines with the iodide is not considered here, but it is expected to happen quite readily on the surface of the COF as it provides favorable multiple chelation sites (Figure 3.4.C). Also, the surface of the porous COF can assist the clustering of iodides and nucleates them to develop as polyiodides such as I_3^- and I_5^- .^[30–32,36] I_2 could also interact with the aqueous electrolyte to form IO_3^- . Synchronously, the hydrated Zn^{2+} ions, $\text{Zn}^{2+}(\text{aq})$, also get stored on the COF (Scheme 3.2.). In support of these understandings, we do not see any substantial current increase in the CV if we employ only the iodide (KI) without Zn^{2+} under comparable three-electrode measurement conditions. Also, the neat ZnI_2 gives a relatively larger current than KI in an aqueous medium, which we believe is due to the superior solubility of the latter. To boot, the inherently soft-acid nature of Zn^{2+} and the soft-base nature of polyiodides should assist their co-storage. For example, our preliminary efforts engaging Al^{3+} (hard-Lewis acid) and iodide indicate that we do not see this synergistic storage (Figure A.3.10.). We and others had observed a similar phenomenon in capacitors where the heteroatoms get enriched with H^+ in acidic electrolytes and sets-up storage centers for such anionic species.^[20–22,27,28] Thus, COF serves as a true dual-ion storage unit. It is interesting to observe that the COF's large pores and spongy structure facilitate the accommodation of even the relatively large solvated Zn^{2+} species. Thus, the adsorbed polyiodide ions create a supplementary redox surface at the electrode–electrolyte interface. Conspicuously, this storage in the crystalline COF can provide a $\text{Zn}^{2+}(\text{aq})$ and polyiodides decorated uniform nano-channel, which would favor the percolation of electrolytes via subtle electrostatic and dispersive forces. Also, it will reduce the charge transfer resistance at the interface. A detailed study is currently underway to identify a superior metal-ion battery based on these fundamental properties of solubility and hard–soft acid–base control.

3.2.7 Measurements on a Flexible Zn-Ion Battery

A high-performance flexible Zn-ion battery was fabricated for practical applications (Figure 3.14.A). The flexible Zn-ion battery can bend to different mechanical states by flexing at different angles, demonstrating a robust construction.

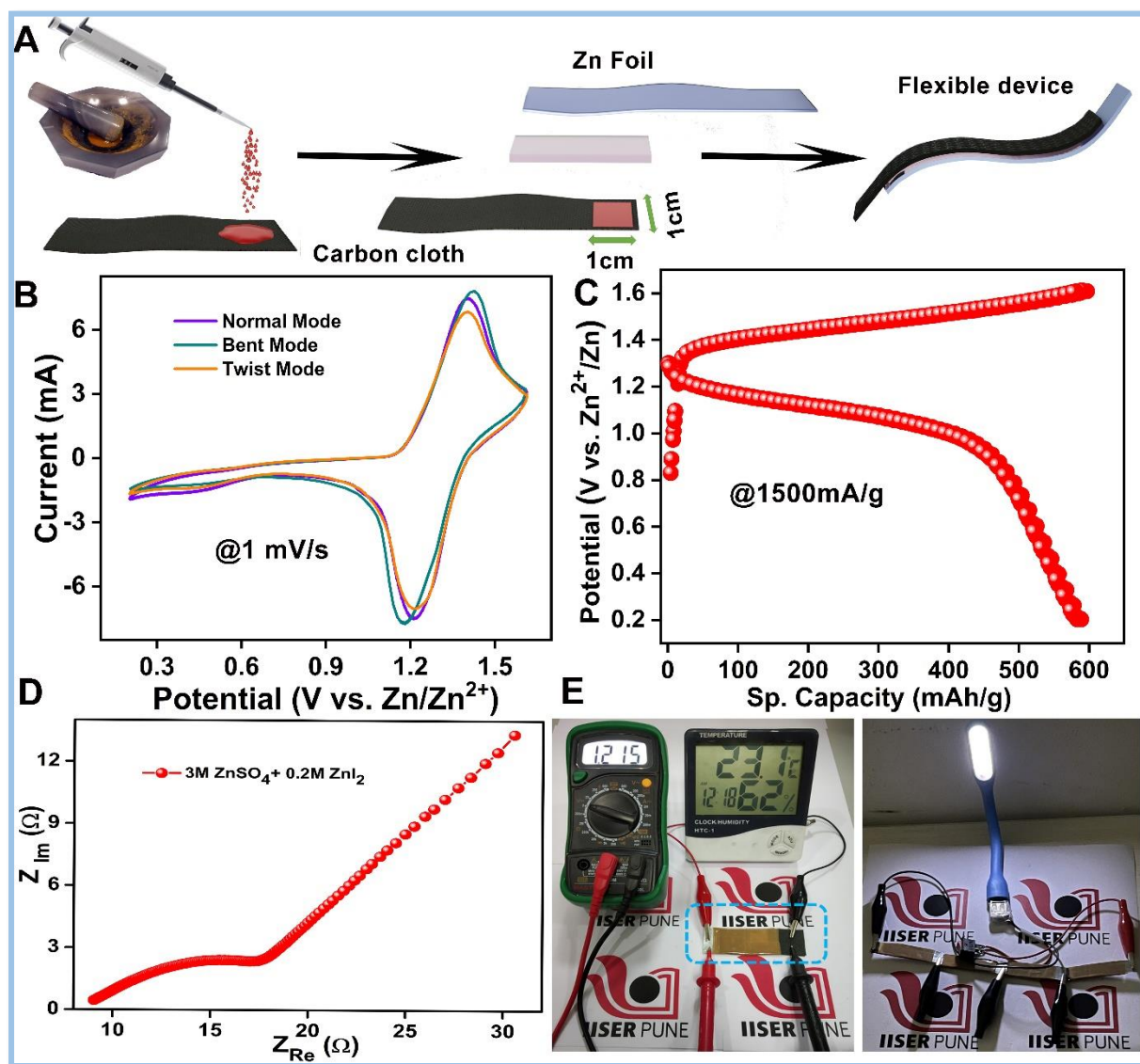


Figure 3.14. (A) Schematic representation of the electrode and the flexible Zn-ion battery Fabrication. (B) Comparative CV plots of the COF-based flexible device measured using 3M ZnSO₄ + 0.2M ZnI₂(aq) as electrolyte at different mechanical states. (C) Galvanostatic charge–discharge curves of the COF-based flexible device measured using 3M ZnSO₄ + 0.2M ZnI₂(aq) as electrolyte. (D) The impedance analysis of flexible device fabricated using 3M ZnSO₄ + 0.2M ZnI₂(aq). (E) The images show that our flexible device is capable of powering a digital watch and table lamp with 8 LEDs and sustains over 11 h without fading.

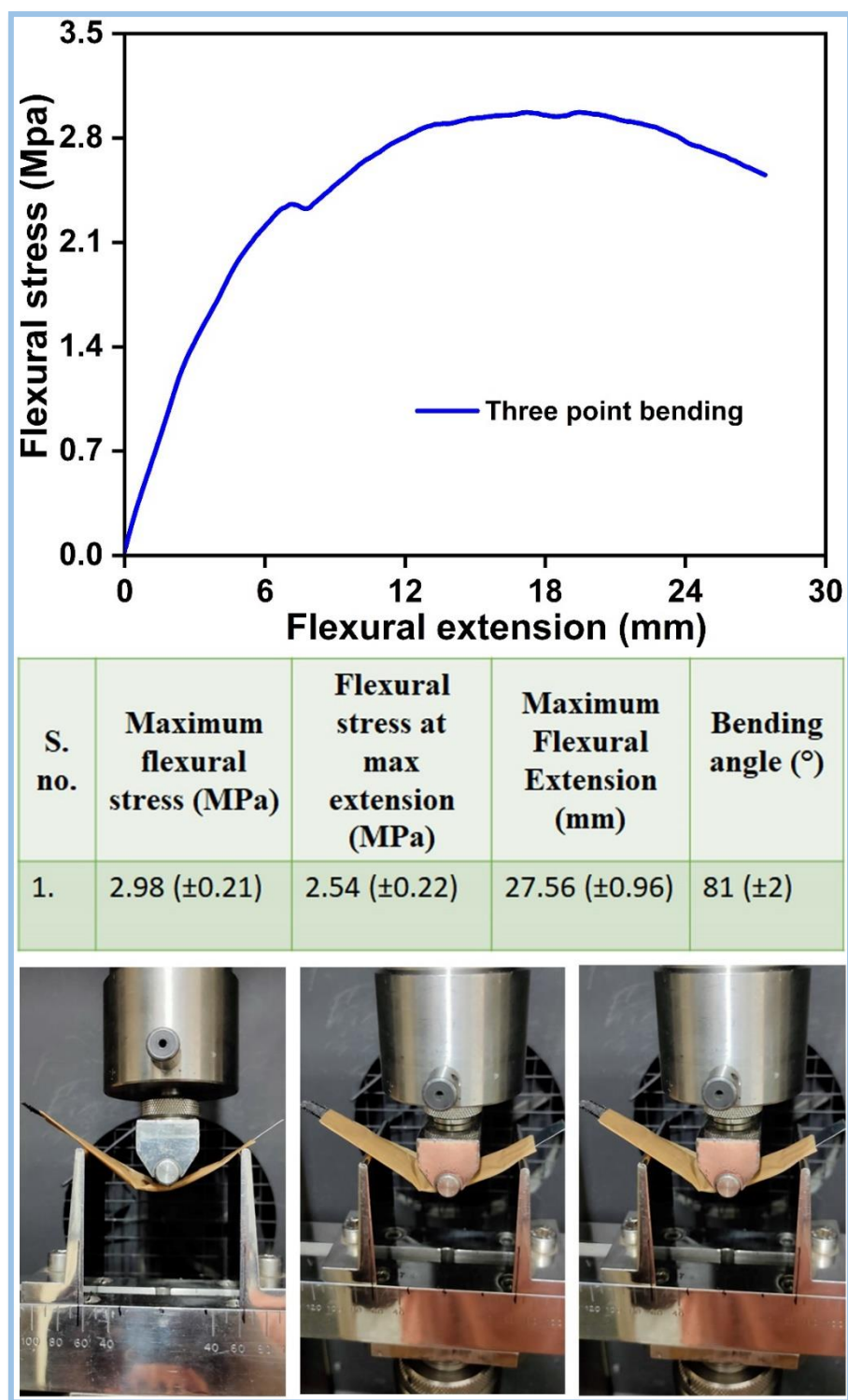


Figure 3.15. The flexural testing of the customized device samples was conducted in 3-point bending mode using Instron Universal Testing Machine. Note: The span length was 6.4 cm and the thickness of the sample was 1.7 mm $\pm$ 0.1 mm. Load cell capacity of 1 kN and strain rate of 13 mm/min were used to deflect the samples up to the maximum deflection point.

The open-circuit voltage value is 1.21 V, almost identical to the coin-cell type Zn-ion battery. The CV curves illustrate the reproducibility of our flexible Zn-ion battery in different bending conditions (Figure 3.14.B, and 3.15.; Figures A.3.19. and A.3.20.). Having flexible devices capable of bending without loss of electrochemical properties is advantageous.^[22,56,57] The charge–discharge profile of the flexible Zn-ion battery is very similar to the Zn-ion coin-cell battery, with slight capacity fading (Figure 3.14.C). Nyquist plot obtained during impedance analysis for the flexible Zn-ion battery is very similar to the Zn-ion coin-cell battery. However, a slight increment in the series resistance (R_s) and the charge transfer resistance (R_{CT}) was observed (Figure 3.14.D). It could be due to the fabrication method of flexible ZIBs. We measured the stress–strain induced on the flexible device using a 3-point bending mode using Instron universal testing machine (Figure 3.15.). The maximum flexural stress of ≈ 3 MPa created a bending angle of 81° . A fit to the linear Hook's region of the stress–strain graph yielded a Young's modulus of 196 MPa, which is comparable to those observed for some of the polymer-SWCNT based ZIB devices.^[58] A single flexible Zn-ion battery was capable enough to power a digital watch and the potential measured simultaneously obtained ≈ 1.2 V. These flexible ZIBs were connected in series to achieve a higher voltage for specific applications, such as lighting the table lamp (Figure 3.14.E, and Figure A.3.20.). These features demonstrated that flexible ZIBs have potential in energy storage and wearable electronics applications with some fabrication improvement.

3.2.8. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed to investigate the constituents generated during the redox process on the coin cell's completely discharged and charged electrode (Figures S33–S37, Supporting Information). The intensity of all XPS spectra from the samples discharged at 0.2 V is higher than those charged at 1.5 V (Figure 3.16.A). The deconvoluted Zn 2p spectrum has peaks of 1046.8 eV for Zn 2p_{1/2} and 1023.7 eV for Zn 2p_{3/2} charged at 1.5V. However, two additional peaks were observed at 1047.6 and 1025.4 eV at discharged at 0.2V, indicating that Zn²⁺ ions interact with IISERP-COF22 (Figure 3.16.A).^[21,59,60] The deconvoluted O 1s spectrum has peaks at 535.30, 533.90, 533.02, and 531.91 eV arising due to the O=C–H⁺, –C=O, S=O, and C–O–H, respectively charged at 1.5V. However, the coin cell discharged at 0.2V, and peaks were observed at 535.30, 534.21, 533.05, and 532.19 eV, indicating that Zn-ions interact with the COF framework's oxygen (Figure 3.16.B). The deconvoluted C1s spectrum has peaks at 284.7, 285.8, and 286.7 eV,

arising due to the C=C, $\text{C}=\text{N}$, and $\text{C}=\text{O}$, respectively, for as-made COF (Figure A.3.21.). The $\text{I } 3d_{5/2}$ and $\text{I } 3d_{3/2}$ levels of the charged and discharged samples did not show much shifts in the binding energy (Figures A.3.22. - A.3.25.), as they are the same species in both cases. The discharge at 0.2 V could not remove all the iodide. However, the relative intensity of the peaks for the charged state (at 1.5 V) was much higher than that of the discharged state. Thus some iodide binds irreversibly, which agrees with the gradual decrease of specific capacity with cycles (Figure 3.12.H).

3.2.9. Spectroscopic Investigations

The exceptional capacity enhancement occurs upon introducing the redox additive, ZnI_2 , into the $\text{ZnSO}_4(\text{aq})$ electrolyte. To further investigate the redox phenomena and generation of active redox intermediate during the charging process, in situ spectro-electrochemical data and regular Ultra-violet- visible light (UV-vis) spectroscopy analysis was carried out to understand the interaction of COF with the generated species.

3.2.9.1. UV-vis Spectroscopy with No Applied Potential

To understand the interaction between COF frameworks with electrolytes, first, the COF was dispersed in the water. This COF constitutes three distinct chromophoric functional groups, giving rise to three absorption peaks (220, 294, and 490 nm) in the UV-vis spectra

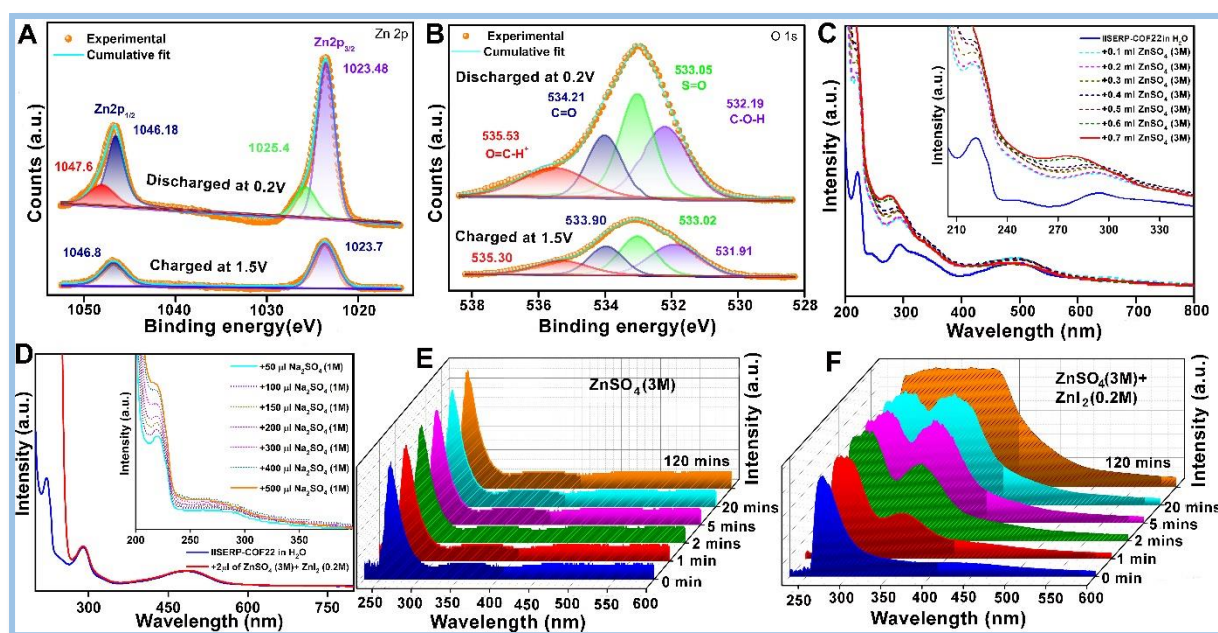


Figure 3.16. (A) Comparative XPS of Zn 2p collected from discharged and charged cathode of coin

cells. (B) Comparative XPS of O 1s collected from discharged and charged cathode of coin cells. (C) Comparative UV–vis spectra collected from the systematic addition of 3 m ZnSO₄(aq) to IISERP-COF22 dispersed in the water. Inset represents the zoomed-in spectra of the same. (D) Comparative UV–vis spectra of IISERP-COF22 dispersed in the water and after the addition of 3M ZnSO₄(aq) + ZnI₂(aq). Inset represents the UV–vis spectra of IISERP-COF22 dispersed in 1M Na₂SO₄(aq). (E) Insitu spectro-electrochemical studies to monitor the change in UV–vis spectra of the IISERP-COF22 during chronoamperometry measurements with 3M ZnSO₄(aq). (F) In situ spectro–electrochemical data to monitor the change in UV–vis spectra of the IISERP-COF22 during chronoamperometry measurements with 3M ZnSO₄ + ZnI₂(aq).

(Figure 3.16.C).^[61] Operando UV–vis data (without applied potential) were collected with a systematic addition of 0.1mL of 3M ZnSO₄(aq) for every 5 min to the COF dispersion. A controlled continuous increment in the intensity of the first absorption peak (at 220 nm) of the UV–vis absorption spectra was observed upon adding 3M ZnSO₄(aq). We observed a notable blue shift (by 15 nm) in the second absorption peak (290nm). While there is no change in the third absorption peak (at 490 nm) (Figure 3.16.C). The increase in the first peak's intensity and the second peak's blue shifting can be attributed to the interaction of ZnSO₄ with the COF. To distinguish the effect of Zn²⁺ and iodide storage/interaction with the COF from the sulphate, we recorded the UV–vis in neat Na₂SO₄ solution (with increasing concentration) and observed only an incremental increase of the peak intensity for the 220 nm peak (Figure 3.16. inset). The 220 nm peak is observed in ZnSO₄ as well as Na₂SO₄, which suggests that this peak is due to the sulfate ions interaction with the COF; while the peak at 294 nm is observed only in the case of ZnSO₄, indicating it has its origin in Zn²⁺ interactions. But, when a small doze (2μL of a 3M ZnSO₄ + 0.2 M ZnI₂) was added, the first peak's intensity shot up beyond the saturation of the UV detector (Figure 3.16.D). Most importantly, we performed the control experiment without employing the COF to indirectly confirm that this activity is preferentially due to the interaction of Zn²⁺ and iodide with the COF.^[62–64] No peaks were observed with the addition of only ZnSO₄. However, when 2μL of ZnI₂ (0.2 mol) was added to the aqueous medium, a sharp peak appeared at ≈260 nm, very similar to the one observed in the presence of the COF (Figure A.3.26).^[37] To gain further clarity, we charged the COF with the Iodide in a three-electrode system and then isolated and washed the COF with copious water and methanol, and dried it. This sample was subjected to XPS analysis to determine the interactions between the iodide and the COF.

3.2.9.2. UV–vis Spectroscopy under Applied Potential

UV–vis findings encourage us to do the UV–vis spectroscopic investigation under potential. A typical three-electrode setup was built to carry out the spectro-electrochemical measurements, where COF coated on a fluorine-doped tin oxide (FTO) plate acts as the working electrode, Ag/AgCl as a reference electrode, platinum as a counter electrode, and $\text{ZnSO}_4(\text{aq})$ and $\text{ZnSO}_4 + \text{ZnI}_2(\text{aq})$ as the electrolyte respectively, inside the UV cuvette (Figure A.3.27.). The entire setup was connected to the ocean optics instrument and the CHI charge–discharge analyzer to observe UV–vis spectral changes in situ. First, a 3M $\text{ZnSO}_4(\text{aq})$ electrolyte was used. Then a chronoamperometry measurement was carried out at 0.8 V over 2 h, and the UV–vis spectrum was recorded at a specific time interval. The first absorption maxima peak of the COF was observed at 264 nm without applied potential. However, there is no noticeable change in the absorption spectra under applied potential even after 2 h (Figure 3.16.E). Finally, 3M $\text{ZnSO}_4(\text{aq}) + 0.2\text{M ZnI}_2$ was employed as the electrolyte inside the UV cuvette. The first absorption maxima peak of the COF was observed at 266 nm without applied potential. Then a chronoamperometry measurement was carried out at 0.8 V over 2 h, and one additional broad peak appeared around 348 nm due to the generation of a new redox species IO_3^- .^[65] Now there is an excess of these IO_3^- species in the medium, due to which the peak intensity is gradually increased and saturated over 2 h (Figure 3.16.F). A crucial change is observed for the COF's original peak at 260 nm upon adding ZnI_2 . The peak shows substantial broadening and an associated redshift. This could be due to the I^- and I_3^- adsorption on the COF and a potential reduction of the IO_3^- at the COF surface. To confirm this, charged COF was extracted, washed with plenty of water and methanol, dried, and its XPS was measured. It was found that most species were I_3^- . It also suggests that the IO_3^- most likely is reduced on the COF during its adsorption, and I_3^- interacts better with the COF. This is expected to be an accelerated process under an applied potential. The Lowest- unoccupied molecular orbital (LUMO) of the COF will get enriched with electrons, and we would have the Highest-occupied molecular orbital (HOMO) of the COF also participating in the process of supplying electrons to the IO_3^- (reduction) to convert it to I_3^- . We notice that the pH of the medium was around 4.5 to 5 during the electrochemical process, which would favor this reduction too. And, I_3^- is known to be a better surface-active species.^[64] Thus what happens is when a potential is applied, the conjugated COF accumulates the electrons on its framework, and this allows the keto groups of the squarate and the amide nitrogens to chelate with Zn^{2+} and also the species such as IO_3^- gets reduced on the COF surface. Notably, even the more conductive N-doped carbon does

not do as well as this COF.^[65] Furthermore, in two separate experiments, we recorded the CV of the COF in the KI and ZnI_2 , and compared it. The current observed in KI was four times lower than that observed for the ZnI_2 . This further confirms that the high current observed for the $\text{ZnSO}_4 + \text{ZnI}_2(\text{aq})$ electrolyte system certainly is due to the favorable synchronized interaction of the COF with the Zn^{2+} and the I_3^- .

3.3 Computational Modeling

We constructed a $2 \times 2 \times 2$ supercell of IISERP-COF22 and included $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and I_3^- in a 1:2 ratio. We enclosed 12 Zn and 24 iodide, and 14 water molecules per unit cell.

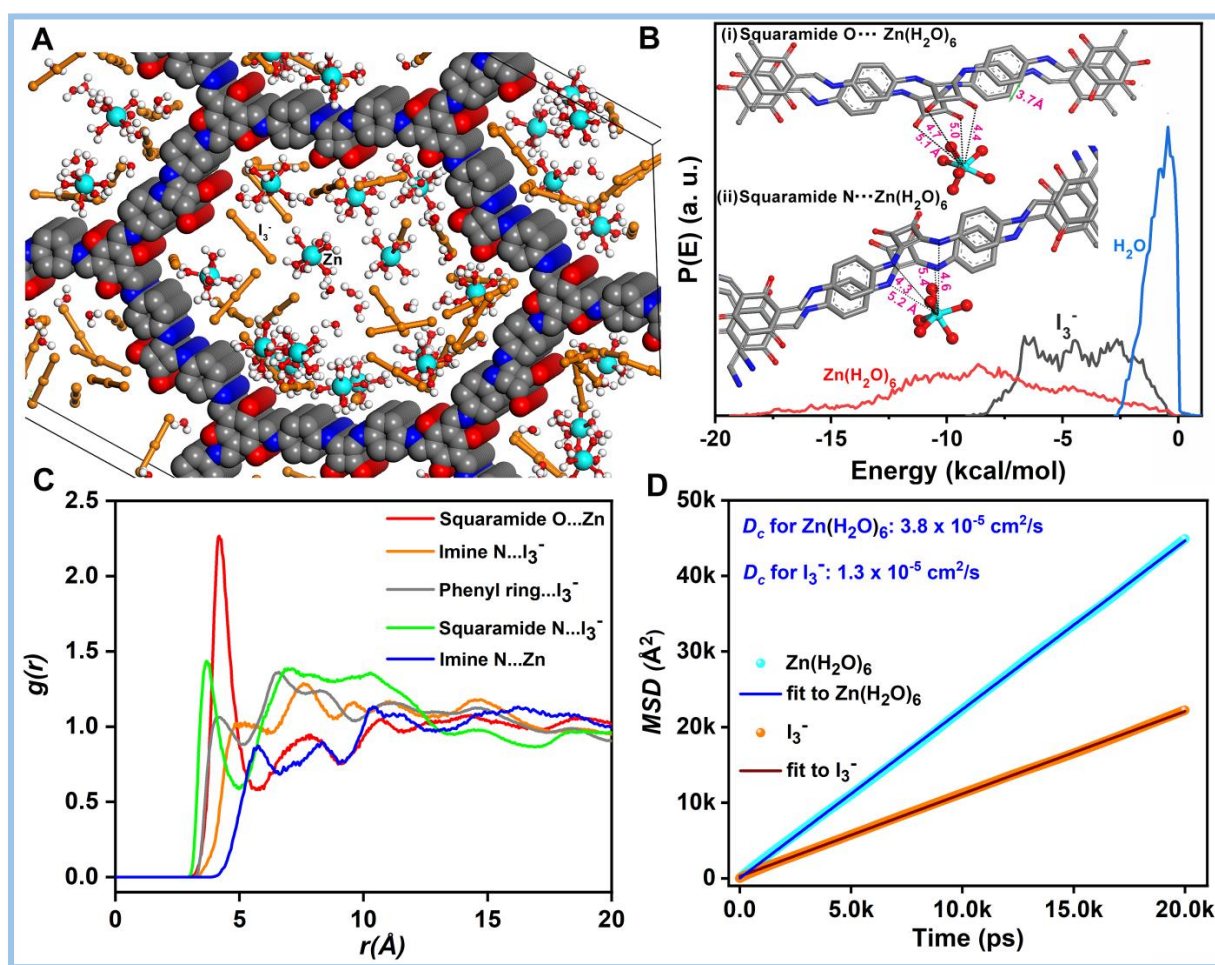


Figure 3.17. (A) snapshot from the 100 ns MD simulation showing the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and I_3^- residing in the pores of the COF. (B) The equilibrated and optimized structure showing the Zn^{2+} and iodides ability to adsorb onto specific sites of the COF. (C) Radial distribution function plots showing the average distances of the interactive groups of the COF with Zn^{2+} and I_3^- . The hexa aqua complex and the

polyiodide are frequently found near the framework atoms. (D) The diffusion coefficient for $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and I_3^- within the framework.

This was optimized using a simulated annealing routine. The lowest energy conformer was then examined using a detailed Molecular Dynamics (MD) simulation (Figure 3.17.A). A 100 ns constant pressure-constant temperature ensemble (NPT) MD simulation (1.0 fs time step; $T=298\text{K}$; $P=1\text{bar}$) was used to reach the equilibrium state; the framework was allowed to relax, but no big change was observed in the lattice parameter of the equilibrated structure. The equilibrated structure was optimized using a 100 ns constant energy- constant volume ensemble (NVE) (1.0 fs time step) to obtain the final configuration at the lowest energy state. Notably, there were no strong covalent interactions in the employed time scales 10 ns, and however, substantial $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and I_3^- were residing proximal to the amide nitrogens and the squarate oxygens (Figure 3.17.B). Their orientations suggest potential chelation, but much longer time scales are required to visualize the loss of water from the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and its subsequent chelation to the framework sites. From about 5000 snapshots out of the 50 000 obtained from the MD, we determined the most favorable distances adopted by the Zn^{2+} ions and the iodides from the framework binding sites using an RDF analysis.^[66] The squarate oxygens seem to be the most prominent in interacting with the Zn^{2+} , while the I_3^- prefers the amide nitrogens (Figure 3.17.C). These agree well with the general trend observed from the MD snapshots. Meanwhile, the diffusion coefficients for the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and the I_3^- were quite high ($10^{-5}\text{cm}^2\text{s}^{-1}$), suggesting very good ion transport within the framework (Figure 3.17.D). Importantly, the relatively bulkier $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ had values comparable to the smaller I_3^- . This is almost certainly due to the former getting assistance from the water molecules via hydrogen bonding.

3.4. Conclusion

In this work, drastic amplification in the charge-storage capacity of ZIB is achieved by coupling a COF-cathode with a redox-active electrolyte. The specialty of the COF is its multiple binding sites capable of chelating with the zinc centers: squaramide- carbonyls; squaramide-amines, and the imine-phenoxide pockets. Meanwhile, the aromatic rings lining the pores are excellent centers for establishing a variety of $\text{C}\cdots\text{I}_3^-$ type of interactions. When the ZnI_2 is introduced into the aqueous system, from the spectro-electrochemistry, it is evident that different iodides

(IO_3^- and I^-) are generated instantly in the solution. When they get adsorbed into the COF-electrode, they are converted to I_3^- under the applied potential. This step constitutes a rapid surge in the current in the CV due to the inclusion of both Zn^{2+} and the polyiodide. The driving force set-up by the pre-coded spongy COF for the large hydrated Zn^{2+} and polyiodide defines the superiority of this COF as an electrode material. This easy percolation of bulky ions through the rich COF channels is registered as low charge transfer and bulk resistance. Importantly, the current generated by this highly polarizable polyiodide species in an aqueous medium is neatly transferable to a flexible battery. And, it works, delivering a very stable potential plateau at 1.3 V with exceptionally high specific capacity (690 mAh g^{-1} at 1.5 mA g^{-1}), sustained even after 6000 cycles, confirming the iodide generation and storage in this aqueous ZIB is not a surge but a sustainable reversible one. The work harbingers the potential of COF-polyiodide combination as an aqueous metal-ion battery and promises huge.

3.5. Acknowledgements

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3.6. References:

- [1] Renewable-energy development in a net-zero world (newsarticle), <https://www.mckinsey.com/industries/electric-power-and-natural-gas/our->

insights/renewable-energy-development-in-a-net-zero-world-land-permits-and-grids, (accessed: October, 2022).

[2] F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu, C. Wang, *Nat. Mater.* 2018, 17, 543.

[3] J. Ming, J. Guo, C. Xia, W. Wang, H. N. Alshareef, *Mater. Sci. Eng.*, R2019, 135, 58.

[4] B. Lee, H. R. Seo, H. R. Lee, C. S. Yoon, J. H. Kim, K. Y. Chung, B. W. Cho, S. H. Oh, *ChemSusChem* 2016, 9, 2948.

[5] J. Zhou, L. Shan, Z. Wu, X. Guo, G. Fang, S. Liang, *Chem. Commun.* 2018, 54, 4457.

[6] T. Xiong, Y. Zhang, Y. Wang, W. S. V. Lee, J. Xue, *J. Mater. Chem. A* 2020, 8, 9006.

[7] Q. Li, K. Ma, C. Hong, Z. Yang, C. Qi, G. Yang, C. Wang, *Energy Storage Mater.* 2021, 42, 715.

[8] G. Fang, J. Zhou, A. Pan, S. Liang, *ACS Energy Lett.* 2018, 3, 2480.

[9] S. Xu, M. Sun, Q. Wang, C. Wang, *J. Semicond.* 2020, 41, 091704.

[10] S. Haldar, R. Kushwaha, R. Maity, R. Vaidhyanathan, *ACS Mater. Lett.* 2019, 1, 490.

[11] S. Haldar, K. Roy, R. Kushwaha, S. Ogale, R. Vaidhyanathan, *Adv. Energy Mater.* 2019, 9, 1902428.

[12] C. R. DeBlase, K. E. Silberstein, T.-T. Truong, H. D. Abruña, W. R. Dichtel, *J. Am. Chem. Soc.* 2013, 135, 16821.

[13] L. Yao, A. Rodríguez-Camargo, M. Xia, D. Mücke, R. Guntermann, Y. Liu, L. Grunenberg, A. Jiménez-Solano, S. T. Emmerling, V. Duppel, K. Sivula, T. Bein, H. Qi, U. Kaiser, M. Grätzel, B. V. Lotsch, *J. Am. Chem. Soc.* 2022, 144, 10291.

[14] D. Chakraborty, P. Shekhar, H. D. Singh, R. Kushwaha, C. Vinod, R. Vaidhyanathan, *Chem. - Asian J.* 2019, 14, 4767.

[15] S. Nandi, S. K. Singh, D. Mullangi, R. Illathvalappil, L. George, C. P. Vinod, S. Kurungot, R. Vaidhyanathan, *Adv. Energy Mater.* 2016, 6, 1601189.

[16] D. Mullangi, V. Dhavale, S. Shalini, S. Nandi, S. Collins, T. Woo, S. Kurungot, R. Vaidhyanathan, *Adv. Energy Mater.* 2016, 6, 1600110.

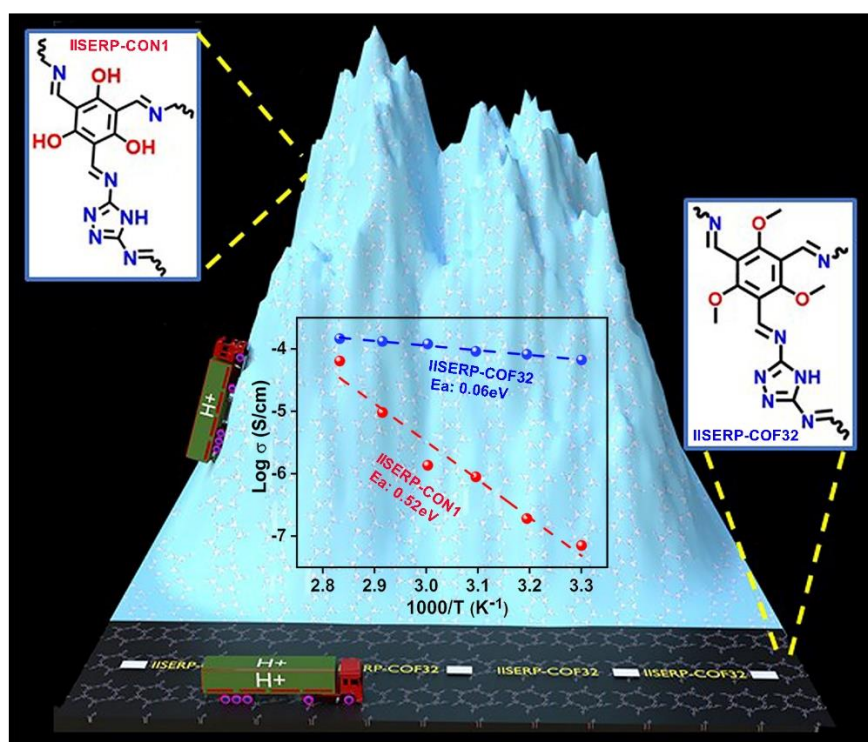
- [17] H. Zhang, L. Zhong, J. Xie, F. Yang, X. Liu, X. Lu, *Adv. Mater.*2021,33,2101857.
- [18] K. W. Nam, H. Kim, Y. Beldjoudi, T.-w. Kwon, D. J. Kim, J. F. Stoddart, *J. Am. Chem. Soc.*2020,142, 2541.
- [19] Z. Lin, L. Lin, J. Zhu, W. Wu, X. Yang, X. Sun, *ACS Appl. Mater. Inter-faces*2022,14, 38689.
- [20] Z. Tie, L. Liu, S. Deng, D. Zhao, Z. Niu, *Angew. Chem. Int. Ed.*2020,59, 4920.
- [21] A. Khayum, M. Ghosh, V. Vijayakumar, A. Halder, M. Nurhuda, S. Kumar, M. Addicoat, S. Kurungot, R. Banerjee, *Chem. Sci.*2019,10,8889.
- [22] W. Wang, V. S. Kale, Z. Cao, S. Kandambeth, W. Zhang, J. Ming, P. T. Parvatkar, E. Abou-Hamad, O. Shekhah, L. Cavallo, M. Eddaoudi, N. Alshareef, *ACS Energy Lett.*2020,5, 2256.
- [23] M. Yu, N. Chandrasekhar, R. K. M. Raghupathy, K. H. Ly, H. Zhang, E. Dmitrieva, C. Liang, X. Lu, T. D. Kühne, H. Mirhosseini, I. M. Weidinger, X. Feng, *J. Am. Chem. Soc.*2020,142, 19570.
- [24] A. Venkatesha, R. Gomes, A. S. Nair, S. Mukherjee, B. Bagchi, A. J. Bhattacharyya, *ACS Sustainable Chem. Eng.*2022,10, 6205.
- [25] D. Ma, H. Zhao, F. Cao, H. Zhao, J. Li, L. Wang, K. Liu, *Chem. Sci.*2022,13, 2385.
- [26] W. Wang, V. S. Kale, Z. Cao, Y. Lei, S. Kandambeth, G. Zou, Y. Zhu, E. Abouhamad, O. Shekhah, L. Cavallo, M. Eddaoudi, H. N. Alshareef, *Adv. Mater.*2021,33, 2103617.
- [27] S. Zheng, D. Shi, D. Yan, Q. Wang, T. Sun, T. Ma, L. Li, D. He, Z. Tao, J. Chen, *Angew. Chem. Int. Ed.*2022,61, e202117511.
- [28] R. Kushwaha, S. Haldar, P. Shekhar, A. Krishnan, J. Saha, P. Hui, C. P. Vinod, C. Subramaniam, R. Vaidhyanathan, *Adv. Energy Mater.*2021,11, 2003626.
- [29] D. Yu, A. Kumar, T. A. Nguyen, M. T. Nazir, G. Yasin, *ACS Sustainable Chem. Eng.*2020,8, 13769.
- [30] Y. Zou, T. Liu, Q. Du, Y. Li, H. Yi, X. Zhou, Z. Li, L. Gao, L. Zhang, X. Liang, *Nat. Commun.*2021,12,1.
- [31] L. Ma, Y. Ying, S. Chen, Z. Huang, X. Li, H. Huang, C. Zhi, *Angew. Chem. Int. Ed.*2021,60, 3791.
- [32] C. Chen, Z. Li, Y. Xu, Y. An, L. Wu, Y. Sun, H. Liao, K. Zheng, X. Zhang, *ACS Sustainable Chem. Eng.*2021,9, 13268.

- [33] X. Li, Z. Wang, J. Sun, J. Gao, Y. Zhao, P. Cheng, B. Aguila, S. Ma, Y. Chen, Z. Zhang, *Chem. Commun.* 2019, 55, 5423.
- [34] J. Huang, Y. Shi, G. Z. Huang, S. Huang, J. Zheng, J. Xu, F. Zhu, G. Ouyang, *Angew. Chem., Int. Ed.* 2022, 61, e202206749.
- [35] S. Sopena, E. Martin, E. C. Escudero-Adan, A. W. Kleij, *ACS Catal.* 2017, 7, 3532.
- [36] K. Jayaramulu, D. P. Dubal, B. Nagar, V. Ranc, O. Tomanec, M. Petr, K. K. R. Datta, R. Zboril, P. Gómez-Romero, R. A. Fischer, *Adv. Mater.* 2018, 30, 1705789.
- [37] V. T. Calabrese, A. Khan, *J. Phys. Chem. A* 2000, 104, 1287.
- [38] E. Taer, A. Putri, R. Farma, R. Taslim, D. Yusra, *Mater. Today: Proc.* 2021, 44, 3241.
- [39] D. Rase, R. Illathvalappil, H. D. Singh, P. Shekhar, L. S. Leo, D. Chakraborty, S. Haldar, A. Shelke, T. G. Ajithkumar, R. Vaidhyanathan, *Nanoscale Horiz.* 2023, 8, 224.
- [40] S. Haldar, M. Wang, P. Bhauriyal, A. Hazra, A. H. Khan, V. Bon, M. A. Isaacs, A. De, L. Shupletsov, T. Boenke, T. Heine, E. Brunner, X. Feng, R. Dong, A. Schneemann, S. Kaskel, *J. Am. Chem. Soc.* 2022, 144, 9101.
- [41] Z. Chen, P. Wang, Z. Ji, H. Wang, J. Liu, J. Wang, M. Hu, Y. Huang, *Nano-Micro Lett.* 2020, 12, 75.
- [42] P. He, M. Yan, G. Zhang, R. Sun, L. Chen, Q. An, L. Mai, *Adv. Energy Mater.* 2017, 7, 1601920.
- [43] N. Qiu, H. Chen, Z. Yang, S. Sun, Y. Wang, *RSC Adv.* 2018, 8, 15703.
- [44] D. Wang, Y. Zhao, G. Liang, F. Mo, H. Li, Z. Huang, X. Li, T. Tang, B. Dong, C. Zhi, *Nano Energy* 2020, 71, 104583.
- [45] P. Liang, J. Yi, X. Liu, K. Wu, Z. Wang, J. Cui, Y. Liu, Y. Wang, Y. Xia, J. Zhang, *Adv. Funct. Mater.* 2020, 30, 1908528.
- [46] Q. Zhang, J. Luan, Y. Tang, X. Ji, H. Wang, *Angew. Chem., Int. Ed.* 2020, 59, 13180. [47] Y. Wang, C. Wang, Z. Ni, Y. Gu, B. Wang, Z. Guo, Z. Wang, D. Bin, J. Ma, Y. Wang, *Adv. Mater.* 2020, 32, 2000338.
- [48] Q. Wang, Y. Liu, P. Chen, *J. Power Sources* 2020, 468, 228401.

- [49] N. Wang, X. Dong, B. Wang, Z. Guo, Z. Wang, R. Wang, X. Qiu, Y. Wang, *Angew. Chem., Int. Ed.* 2020, 59, 14577.
- [50] Z. Guo, Y. Ma, X. Dong, J. Huang, Y. Wang, Y. Xia, *Angew. Chem., Int. Ed.* 2018, 130, 11911.
- [51] G. Dawut, Y. Lu, L. Miao, J. Chen, *Inorg. Chem. Front.* 2018, 5, 1391.
- [52] J. Chang, H. Li, J. Zhao, X. Guan, C. Li, G. Yu, V. Valtchev, Y. Yan, S. Qiu, Q. Fang, *Chem. Sci.* 2021, 12, 8452.
- [53] H. Li, J. Chang, S. Li, X. Guan, D. Li, C. Li, L. Tang, M. Xue, Y. Yan, V. Valtchev, S. Qiu, Q. Fang, *J. Am. Chem. Soc.* 2019, 141, 13324.
- [54] Z. Zhang, X. Dong, J. Yin, Z.-G. Li, X. Li, D. Zhang, T. Pan, Q. Lei, X. Liu, Y. Xie, F. Shui, J. Li, M. Yi, J. Yuan, Z. You, L. Zhang, J. Chang, H. Zhang, W. Li, Q. Fang, B. Li, X.-H. Bu, Y. Han, J. *Am. Chem. Soc.* 2022, 144, 6821.
- [55] Y. Qiu, A. H. Winter, *J. Org. Chem.* 2020, 85, 4145.
- [56] Z. Zhao, R. Wang, C. Peng, W. Chen, T. Wu, B. Hu, W. Weng, Y. Yao, J. Zeng, Z. Chen, P. Liu, Y. Liu, G. Li, J. Guo, H. Lu, Z. Guo, *Nat. Commun.* 2021, 12, 6606.
- [57] S. Haldar, D. Rase, P. Shekhar, C. Jain, C. P. Vinod, E. Zhang, L. Shupletsov, S. Kaskel, R. Vaidhyanathan, *Adv. Energy Mater.* 2022, 12, 2200754.
- [58] M. Yao, Z. Yuan, S. Li, T. He, R. Wang, M. Yuan, Z. Niu, *Adv. Mater.* 2021, 33, 2008140.
- [59] M. Futsuhara, K. Yoshioka, O. Takai, *Thin Solid Films* 1998, 322, 274.
- [60] M. B. Haider, *Nanoscale Res. Lett.* 2017, 12, 5.
- [61] P. Lasitha, S. Dasgupta, G. N. Patwari, *ChemPhysChem* 2020, 21, 1564.
- [62] S. Lakshmi, A. Jayakrishnan, *J. Appl. Polym. Sci.* 2002, 84, 493.
- [63] A. Rostami, A. Ebrahimi, J. Husband, M. U. Anwar, R. Csuk, A. Al-Harrasi, *Eur. J. Chem.* 2020, 2020, 1881.
- [64] S. Saha, S. Roy, P. Mathi, J. A. Mondal, *J. Phys. Chem. A* 2019, 123, 2924.
- [65] F. Wang, J. Tseng, Z. Liu, P. Zhang, G. Wang, G. Chen, W. Wu, M. Yu, Y. Wu, X. Feng, *Adv. Mater.* 2020, 32, 2000287.

[66] N. K. Jena, I. Josefsson, S. K. Eriksson, A. Hagfeldt, H. Siegbahn, O. Björneholm, H. Rensmo, M. Odelius, Chem. - Eur. J. 2015, 21, 4049.

Transformation of Covalent Organic Nanosheets to Covalent Organic Framework via Molecular Design to Achieve High Room Temperature Proton Conduction



4.1. Introduction:

Due to growing concerns about the shortage of fossil fuels and environmental degradation, hydrogen fuel cells have been identified as an essential source of renewable and clean energy, with proton exchange membrane (PEM) fuel cells being the most extensively researched. PEM fuel cells facilitate the utilization of hydrogen for portable applications.^[1] PEM constitutes the heart of fuel cells. Therefore, the development of PEM materials showing high and stable proton conductivity is of critical importance to the operation of fuel cells.^[2] However, the high manufacturing cost of Nafion and its limited working conditions demand further material development. In the past few decades, metal–organic frameworks (MOFs) have drawn much attention due to their highly ordered crystalline structures and easily modified chemical compositions appropriate for high proton conductivity.^{[3] [4] [5]} Nevertheless, MOFs as proton-conductive materials need to overcome several challenges before utilization as proton exchange membranes. Such as insufficient hydrothermal stability, inadequate mechanical strength, difficulty in forming membranes, etc.^{[6] [7]} Covalent Organic Frameworks (COFs) are a class of porous materials that have attracted attention in recent years due to their high surface area, tunable pore size, and excellent stability.^{[8] [9] [10]} They are constructed from organic building blocks with robust covalent bonds. Some properties of COFs, such as excellent chemical stability, a large specific surface area, and a designable pore environment, have made them ideal materials for diverse applications such as catalysis, gas adsorption, batteries, supercapacitors, etc.^{[11] [12] [13]} One of the unique features of COFs is their ability to conduct protons, making them promising materials for applications in proton-conducting membranes, fuel cells, and other electrochemical devices.^{[14] [15]} COFs ion conductors have recently received much attention due to their insulating properties and intrinsic features in fuel cells and solid-state ion batteries. Ordered one-dimensional channels help in fast percolations of proton and carrier retaining capacity. Donglin Jiang and co-worker synthesized the chemically stable COF and doped imidazole and triazole into the pore of COF, achieved the proton conductivities of 1.79×10^{-3} and 7.0×10^{-4} respectively.^[16] Similarly, the imidazole and phenazine moieties were introduced into the framework to achieve high proton conductivities using different strategies.^{[17] [18] [19]} Enhancing proton conductivity and ensuring adequate mechanical flexibility in polymer electrolyte membranes are crucial factors for improving the efficiency of proton exchange membrane (PEM) fuel cells. Currently, Nafion and Nafion-based composite polymers have exhibited remarkable proton conducting capabilities, positioning them as leading candidates for proton exchange membranes in low-temperature PEM-based fuel cells.

However, the lack of comprehensive understanding regarding the structure-property relationships of these polymers and polymer-based composites poses a significant challenge to their further development. In this work, we propose to investigate the relationships between CON vs. COF for proton conduction application via molecular-level tuning with hydroxyl vs. methoxy functional groups, respectively. The CONs can be viewed as a disordered variant derived from Covalent Organic Frameworks (COFs), manifesting as a two-dimensional material that grows in layers with substantial porosity. It can be easily exfoliated from COFs into single/few-layered nanosheets (CONs). Different strategies exist for synthesized exfoliated nanosheets according to the weak/strong interlayer interaction. Nevertheless, distinct varieties of nanosheets exist that are referred to as self-exfoliated nanosheets. These can be synthesized by selecting the building unit in a manner that diminishes interlayer interactions, preventing their growth as Covalent Organic Frameworks (COFs). In this case due to the inclusion of the methoxy group, the long-range ordering has been achieved along with the crystallinity. Finally, a self-standing, flexible, porous, COF membrane (COFM) was utilized as a proton exchange membrane (PEM) for fuel cell application. Covalent organic framework membranes (COFMs) are self-standing, flexible membranes made of COF. The powder nature of COF hinders the development of COF-based membranes and limits technological advancement. Subsequently, various fabrication methods for COF-based membranes are categorized into pure COF membranes, and COF mixed matrix membranes.

4.2. Results:

4.2.1. Synthesis of IISERP-CON1 and IISERP-COF32:

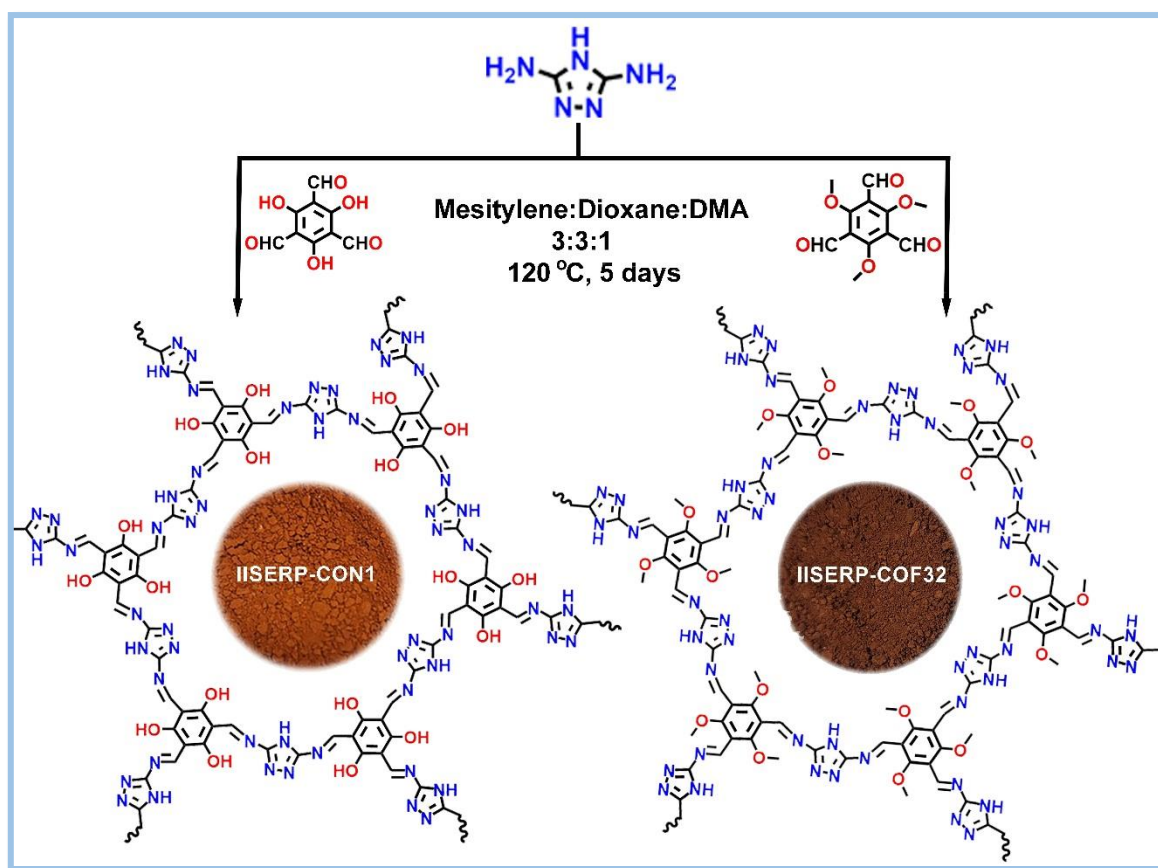


Figure 4.1. The synthesis of IISERP-CON1 and IISERP-COF32.

Synthesis of IISERP-CON1: As reported from our lab,^[20] 1,3,5-triformylphloroglucinol (90mg, 0.42mmol) and 3,5-diamino-1,2,4-triazole (45mg, 0.45mmol) were weighed into a Pyrex tube and dissolved in dioxane (3.0 mL), dimethylacetamide (1.0 mL) and mesitylene (3.0 mL) were added and stirred for 15 minutes. Following this, 1.0 mL of 6M aqueous acetic acid was added. Then the Pyrex tube was sealed and flash-frozen in a liquid nitrogen bath. It was kept in an oven at 120°C for 5 days. After the reaction, the mixture was filtered as a reddish-brown precipitate, which was washed with hot DMF, dioxane, MeOH, acetone, THF and dried in the hot oven at 80°C (85%, isolated yield). This reddish-brown solid was subjected to a Soxhlet extraction using DMA/THF as solvent. (Formula for IISERP-CON1: $C_{24}N_{15}O_6H_{15}$, M. Wt. 610g/mol).

Synthesis of IISERP-COF32: 1,3,5-triformyl trimethoxybenzene^[21] (77mg, 0.3mmol) and 3,5-diamino-1,2,4-triazole (45mg, 0.45mmol) were weighed into a Pyrex tube and dissolved in dioxane (3.0 mL), dimethylacetamide (1.0 mL) and mesitylene (3.0 mL) were added and stirred for 15 minutes. Following this, 1.0 mL of 6M aqueous acetic acid was added. Then the Pyrex

tube was sealed and flash-frozen in a liquid nitrogen bath. It was kept in an oven at 120°C for 5 days. After the reaction, the mixture was filtered as a reddish-brown precipitate, which was washed with hot DMF, dioxane, MeOH, acetone, and THF and dried in the hot oven at 80°C (85%, isolated yield). This reddish-brown solid was subjected to a Soxhlet extraction using DMA/THF as solvent.

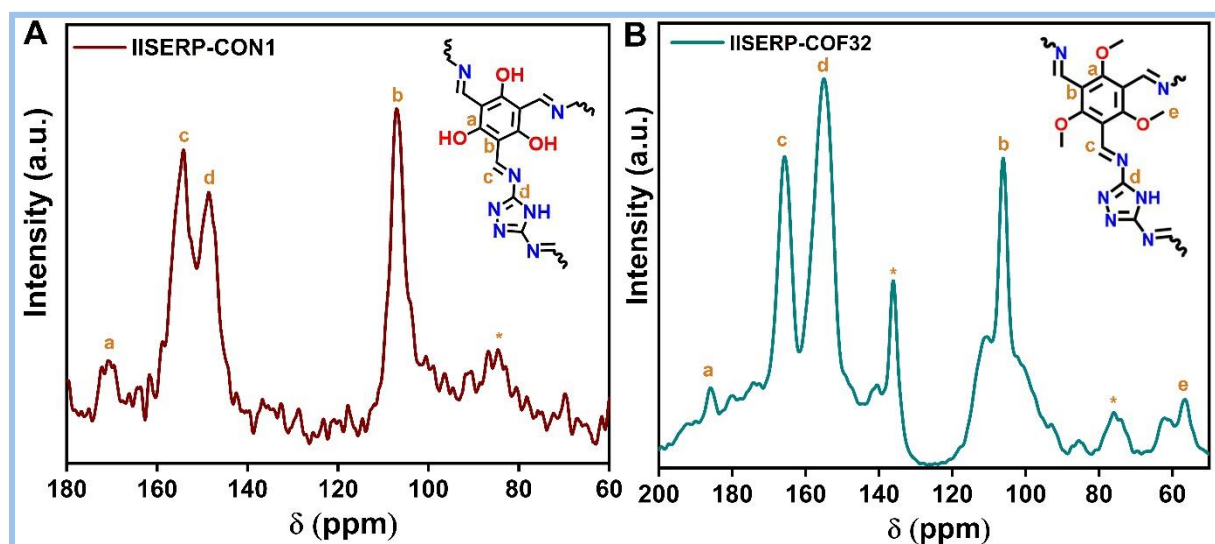


Figure 4.2. (A) CP MAS ^{13}C -NMR spectra of the IISERP-CON1 at 500 MHz a, b, c, and d are the positions of the corresponding peaks obtained from the NMR data. (B) CP MAS ^{13}C -NMR spectra of the IISERP-COF32 at 500 MHz a, b, c, d, and e are the positions of the corresponding peaks obtained from the NMR data

The presence of suitable peaks corresponding to the Schiff bonds ($-\text{C}=\text{N}-$) in the solid-state NMR and infrared (IR) spectra of the CON and COF. (Figures 4.2. and 4.3.). It also surmises that the monomers retain their functional group integrity during polymerization.

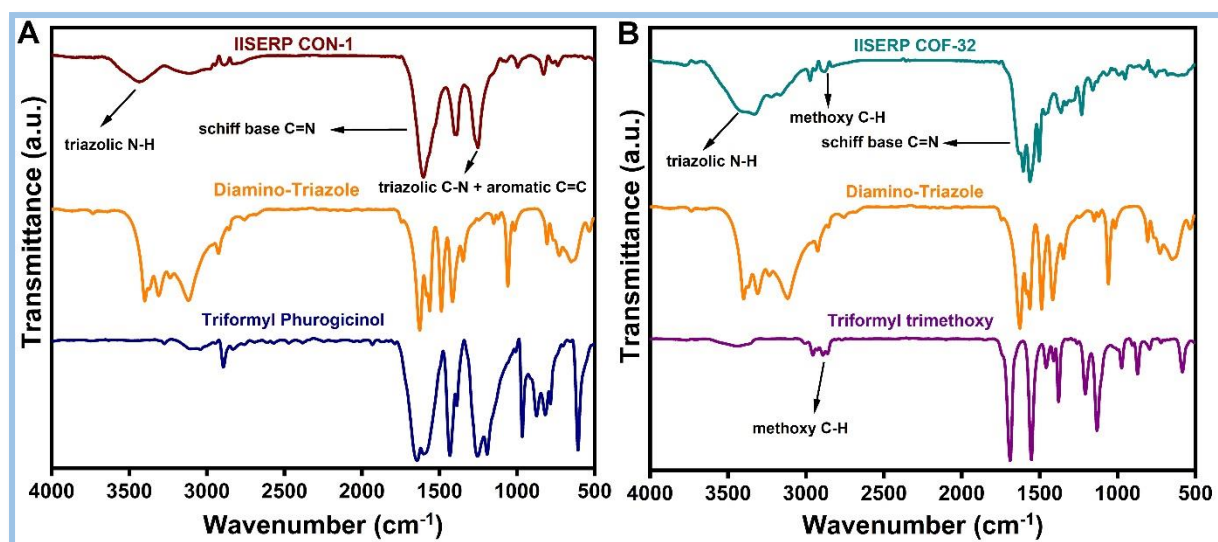


Figure 4.3. (A, B) Comparison of the Fourier transform infrared (FT-IR) spectra of IISERP-CON1, IISERP-COF32, diamino-triazole, triformyl trimethoxy benzene, and triformyl phloroglucinol.

4.2.2. Improved crystallinity of IISERP-COF32 over IISERP-CON1:

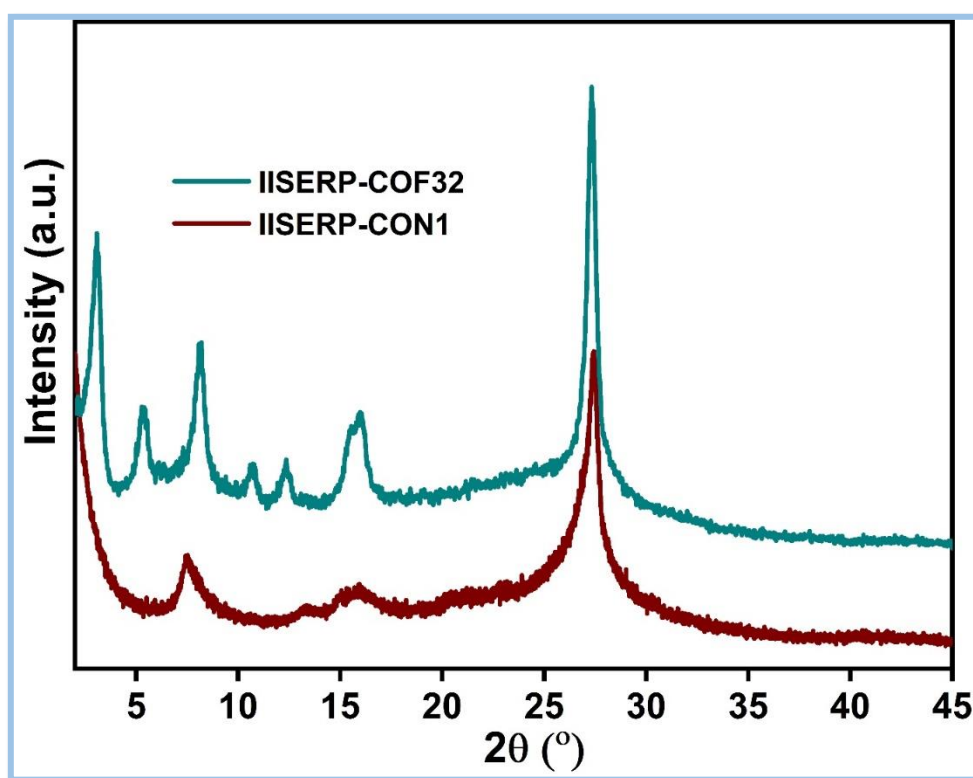


Figure 4.4. Comparative Powder X-ray diffraction (PXRD) of IISERP-CON1 and IISERP-COF32.

The crystallinity of these materials was examined by Powder X-ray diffraction (PXRD) instrument (Figure 4.4.). A very high degree of crystallinity was observed in the PXRD pattern for the IISERP-COF32, attributed to a very long-ordered structure. However, the nanosheets (IISERP-CON1) do not contain sufficient layers to give rise to intense peaks in the powder X-ray diffraction (PXRD) pattern compared to COF. Furthermore, the CON and COF formation was confirmed by solid-state nuclear magnetic resonance (SSNMR) and IR spectroscopy (Figures 4.2. and 4.3.).

4.2.3. Characterization: Porosity and morphology

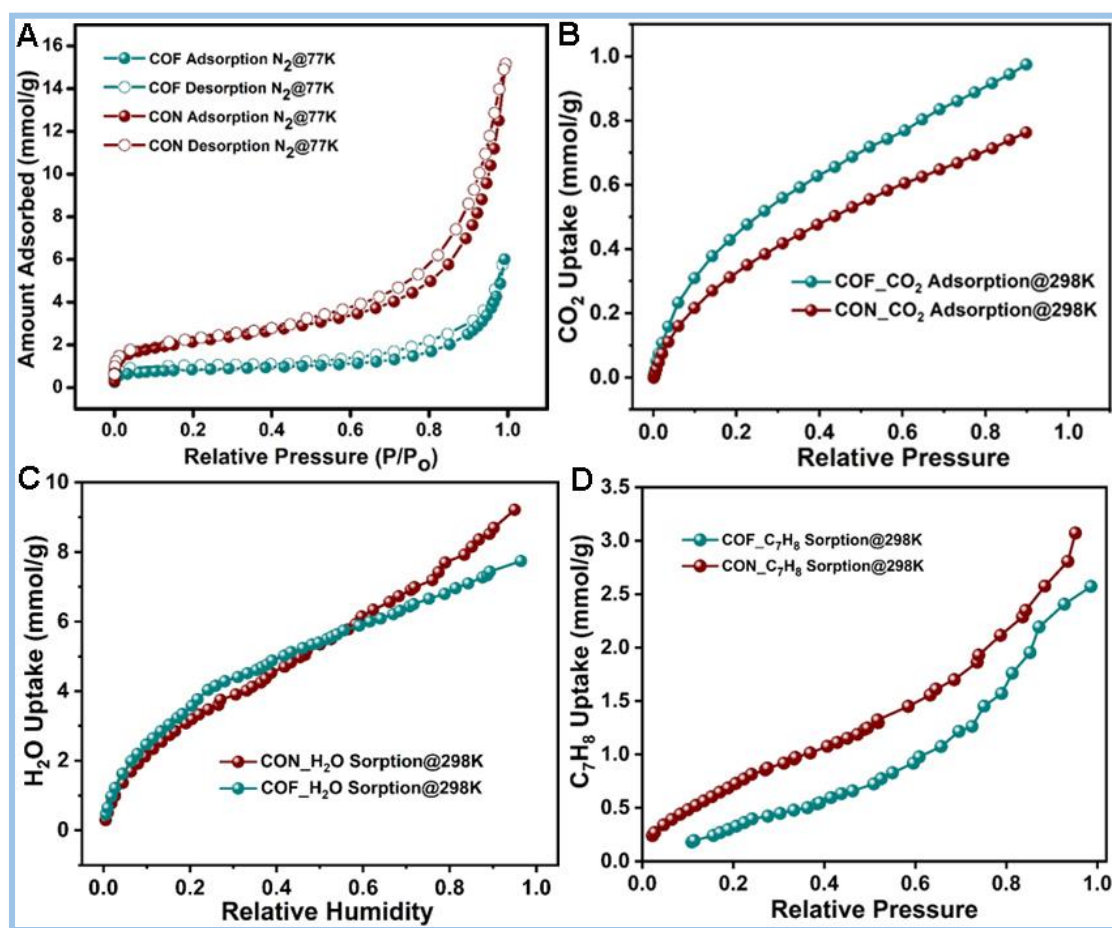


Figure 4.5. (A) Comparative N₂ adsorption isotherms of IISERP-CON1 and IISERP-COF32 at 77 K. (B) Comparative CO₂ adsorption isotherms of IISERP-CON1 and IISERP-COF32 at 298K. (C) Comparative H₂O sorption isotherms of IISERP-CON1 and IISERP-COF32 at 298K. (D) Comparative toluene sorption isotherms of IISERP-CON1 and IISERP-COF32 at 298K.

The as-synthesized CON/COF yielded a completely reversible type-II nitrogen adsorption isotherm (Figure 4.5.A). The N_2 uptake of CON is slightly higher compared to COF suggesting the presence of methoxy group in the COF creates a hinderance for incoming N_2 . However, the CO_2 uptake of COF is slightly higher compared to CON suggesting the presence of methoxy group in the COF creates a hydrophobic shielding and reduced lone pair-lone pair repulsion of framework oxygen and oxygen of incoming CO_2 (Figure 4.5.B). To comprehend the hydrophilic and hydrophobic nature of CON and COF, we conducted the water and toluene sorption experiments (Figure 4.5.C and 4.5.D). The toluene sorption isotherms suggest poorer adsorbate-adsorbent interactions at low pressures. Therefore, these materials have good wettability, advantageous for proton conduction under humidity. Type I adsorption water sorption isotherms suggests good adsorbate-adsorbent interactions at low pressures. Therefore, these materials have good wettability, advantageous for proton conduction under humidity. To check the chemical stability, the COF was soaked in $HCl(6M)$, $H_2SO_4(6M)$, $H_3PO_4(6M)$, and $NaOH(6M)$, respectively, and the PXRD patterns remain intact (Figure A.4.1.). Further, thermogravimetric analysis showed the thermal stability of the CON and COF (stable up to $\approx 400^\circ C$) (Figure A.4.2.). COF showed stable and higher plateau compared to CON.

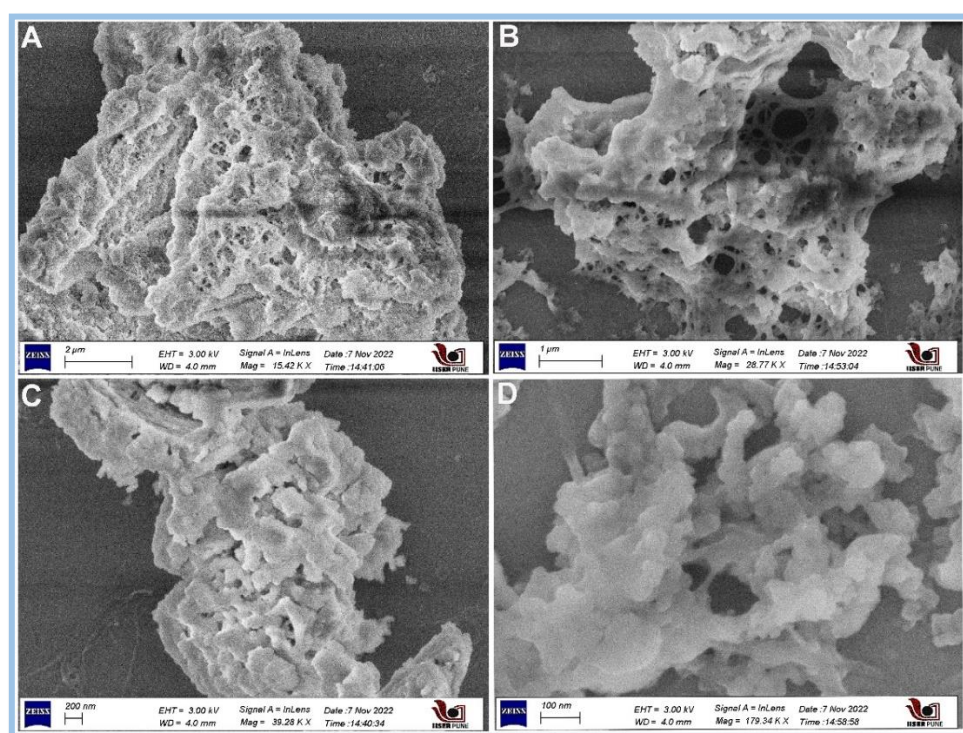


Figure 4.6. (A) FESEM images of IISERP-CON1 at different resolutions. It shows a flaky sheet-like morphology. At the lower resolution, many sheets clubbed together and formed staked sheet morphology. Whereas at higher resolution, the presence of tubular block morphology can be seen.

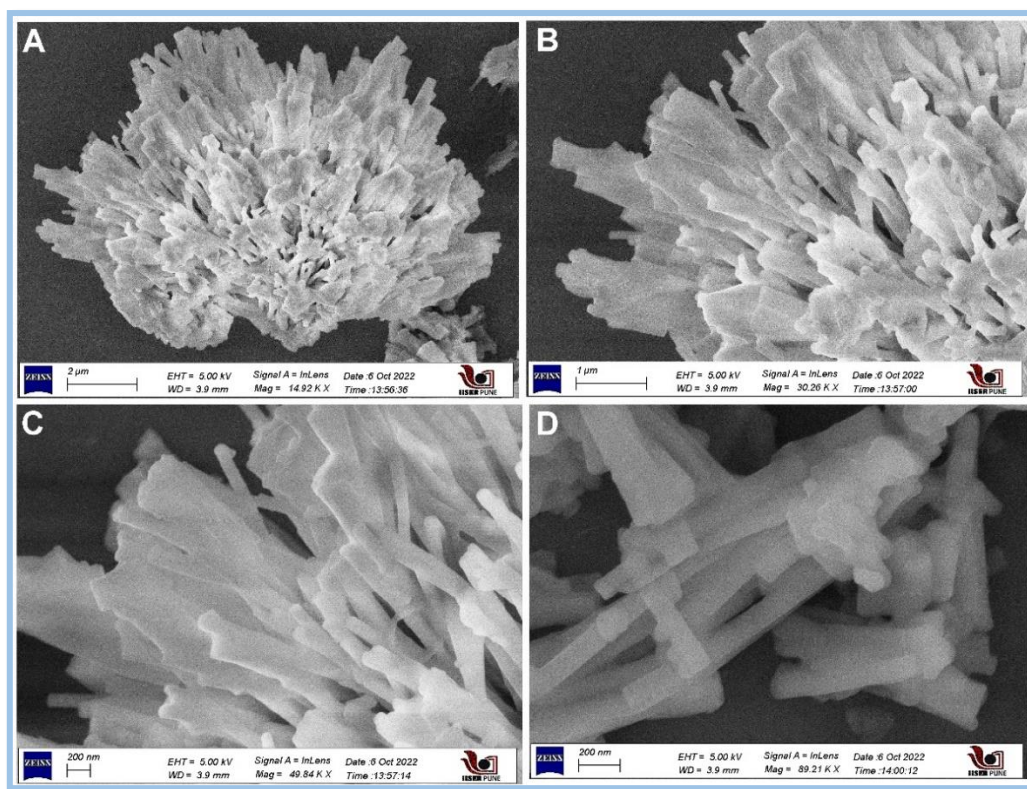


Figure 4.7. FESEM images of IISERP-COF32 at different resolutions. It shows flaky COF rod-like morphology. At the lower resolution, many rods clubbed together and formed a dendritic morphology. Whereas at higher resolution, the presence of tubular block or rod-like morphology can be seen.

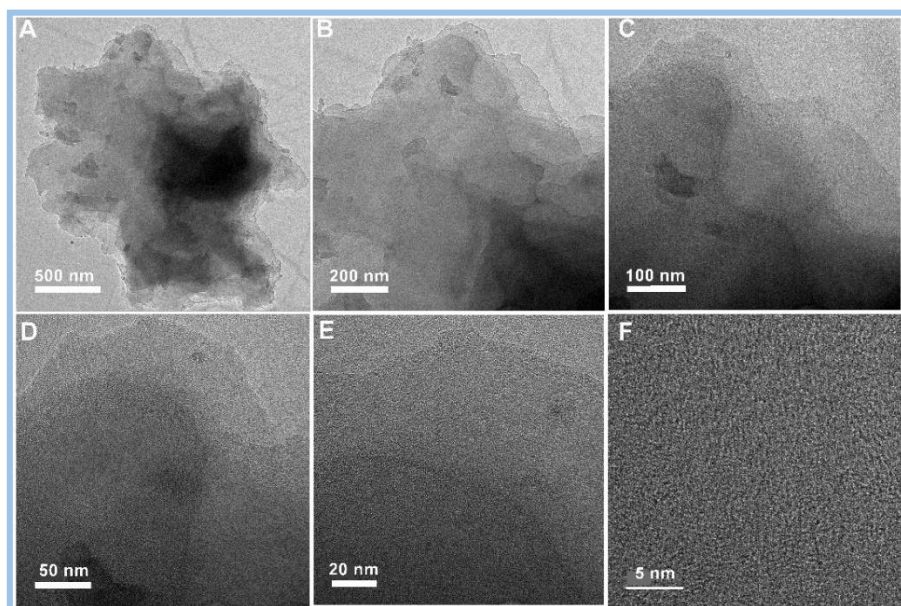


Figure 4.8. HRTEM images of IISERP-CON1 at different resolutions. It shows flaky sheet-like morphology. At the lower resolution, many rods clubbed together and formed staked sheet morphology. Whereas at higher resolution, the presence of tubular morphology can be seen.

Under the FE-SEM, the CON shows a flaky cotton-like morphology. However, the COF has rod-like morphology at different resolution scales (Figures 4.6. and 4.7.). In addition, the HR-TEM images of the CON show the morphology of exfoliated COF with thin layers stacked on each other, rod-like morphology obtained for COF (Figures 4.8. and 4.9.). In a higher-resolution TEM image, the fine porous surface of the nanosheets could be observed, but the lattice fringes are observed for COF (Figures 4.8. and 4.10.). It could be assigned to different d spacing. Many diffraction spots were observed in the selected area of electron diffraction (SAED) for COF. Another strong evidence for the presence of a few-layer-thin nanosheet (CON) vs. multi-layer-thick framework materials (COF) comes from the atomic force microscopy (AFM) studies. The height profile and the dimensions extracted from the AFM images of a drop-casted sample showed thicknesses of ≈ 4 -10 nm for CON, but the thicknesses observed for COF were ≈ 100 -600 nm (Figure 4.11.).

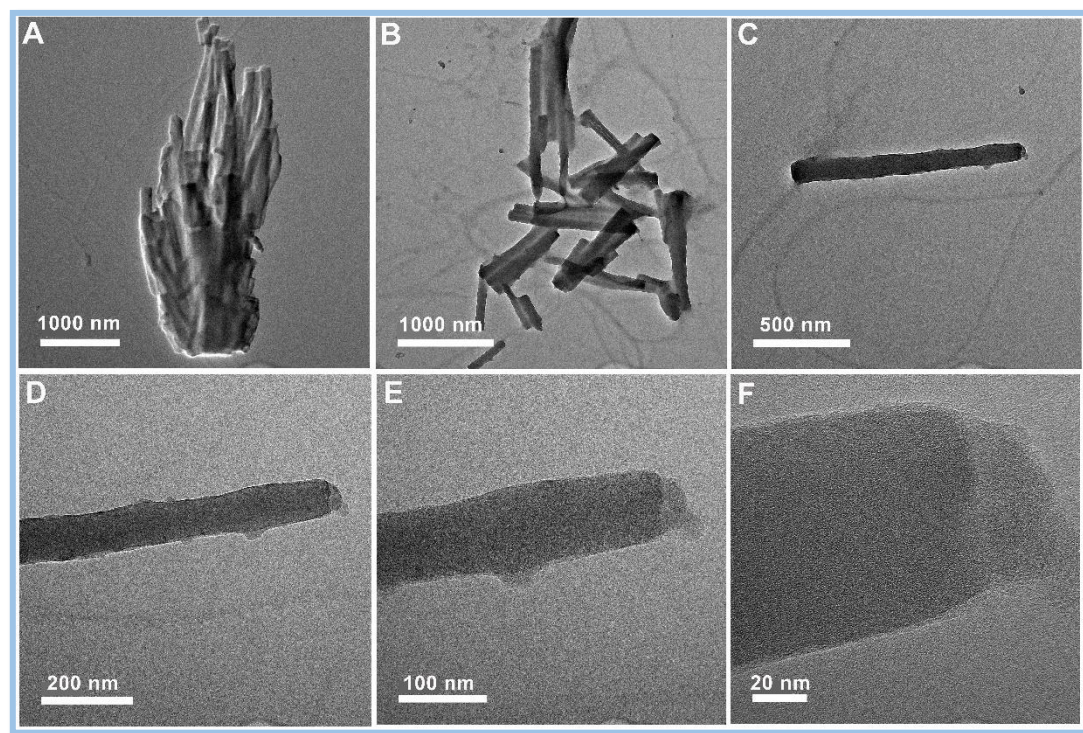


Figure 4.9. HRTEM images of IISERP-COF32 at different resolutions. It shows flaky COF rod-like morphology. At the lower resolution, many rods clubbed together and formed a dendritic morphology. Whereas at higher resolution, the presence of tubular block or rod-like morphology can be seen.

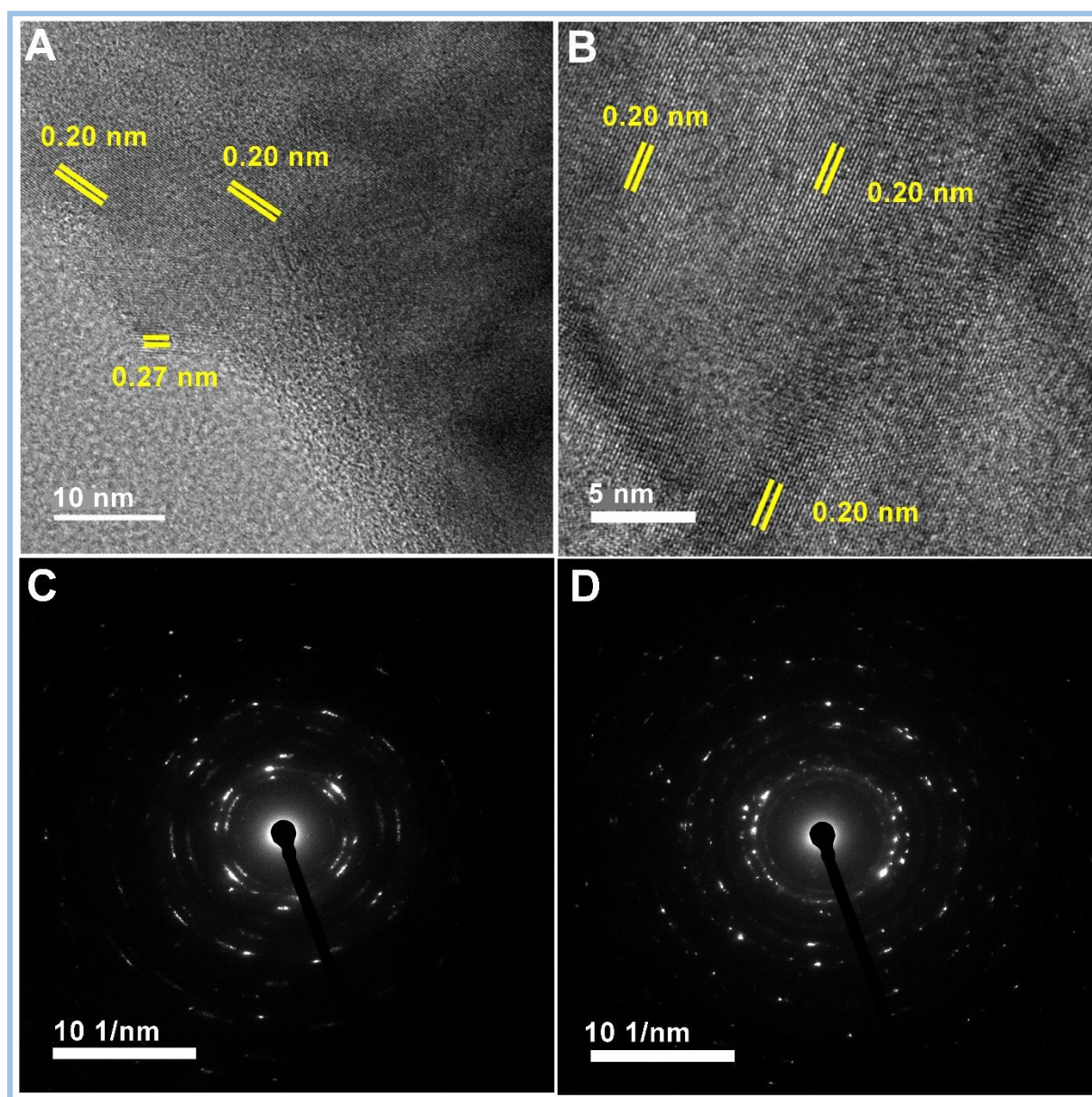


Figure 4.10. FETEM images of IISERP-COF32 at different resolutions. It shows flaky COF rod-like morphology. At the lower resolution, many rods clubbed together and formed a dendritic morphology. Whereas at higher resolution, the presence of tubular block or rod-like morphology can be seen.

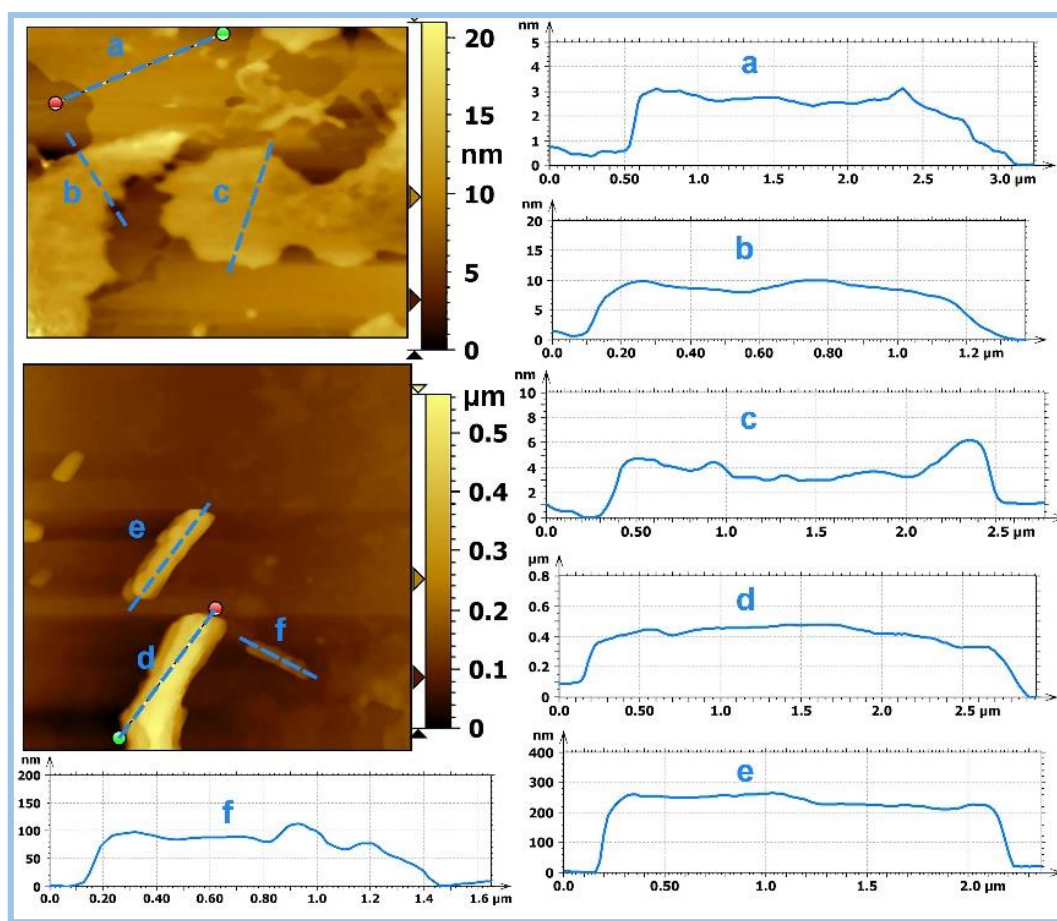


Figure 4.11. The AFM image IISERP-CON1 shows the thickness of the drop-casted sample and the height profile plot ranges of ≈ 4 –10 nm. (C) The AFM image IISERP-COF32 shows the thickness of the drop-casted sample and the height profile plot ranges of ≈ 100 –600 nm.

4.2.4. Synthesis of H_3PO_4 @IISERP-CON1 and H_3PO_4 @IISERP-COF32

The dried powder samples of IISERP-CON1 and IISERP-COF32 (180 mg) were weighted to an Agate mortar, and then 60 μL of 85 wt% phosphoric acid was added to the above mortar. Then 3 mL ethanol was added to it. After smooth manual grinding in a mortar and pestle for 30 minutes, keep in the normal oven to evaporate the ethanol. The solids were collected and dried at 90 $^\circ\text{C}$ under a vacuum for 10 hours. The phosphoric acid doped samples were denoted as H_3PO_4 @IISERP-CON1 and H_3PO_4 @IISERP-COF32.

4.2.5. Impedance analysis

Impedance analysis was carried out with and without acid-loaded samples.

The hydrogen ion conductivity (σ) of the IISERP-CON1, H_3PO_4 @IISERP-CON1, IISERP-COF32, and H_3PO_4 @IISERP-COF32 were analyzed by the electrochemical impedance

spectroscopy method from a frequency range of 1 Hz–10 MHz using the Solartron Impedance Analyzer. For this, IISERP-CON1, $\text{H}_3\text{PO}_4\text{@IISERP-CON1}$, IISERP-COF32 and $\text{H}_3\text{PO}_4\text{@IISERP-COF32}$ were made into a pelletized form. The conductivity measurements were carried out three times on different pellet thicknesses (0.6 to 0.8 mm) and diameters of 10 mm to validate the consistency in the obtained results. Before each measurement, the sample was equilibrated at a certain temperature and humidity for 2 h throughout the experiment. The hydrogen ion conductivity of the pellet was measured from room temperature (25 °C) to 80 °C in relative humidity (RH) of 95% and calculated using the following equation.

$$\sigma \text{ (S cm}^{-1}\text{)} = \frac{l}{RA}$$

where l is the thickness of the pellet (cm), R is the resistance of the sample (Ω) obtained from the x-axis intercept, and A is the cross-sectional area of the pellet (cm^2).

4.2.5.1. Temperature-dependent hydrogen ion conductivity analysis of IISERP-CON1 and IISERP-COF32

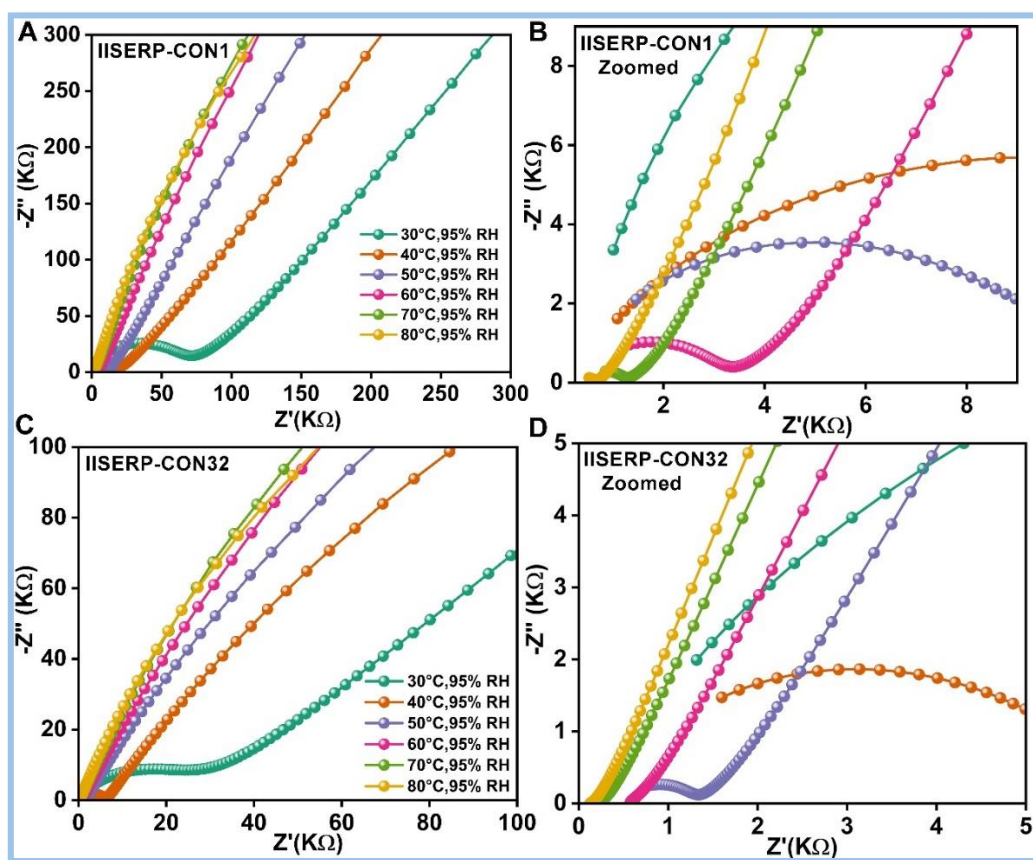


Figure 4.12. (A) Comparative Nyquist plots of IISERP-CON1 (without acid loading) were measured with circular pellets under 95% RH at different temperatures. (B) Comparative zoomed Nyquist plots of IISERP-CON1 (without acid loading). (C) Comparative Nyquist plots of IISERP-COF32 (without acid loading) were measured with circular pellets under 95% RH at different temperatures. (D) Comparative zoomed Nyquist plots of IISERP- COF32 (without acid loading).

The presence of hydrogen in the heteroatoms such as N-H and O-H in the backbone of IISERP-CON1 and IISERP-COF32 act as proton conducting sites. The proton conductivities were measured from room temperature 25 to 80 °C under 95% RH (relative humidity) with the pellets at similar operating conditions. The Nyquist plots show the proton conductivities varying from $7.04 \times 10^{-7} \text{ S cm}^{-1}$ to $7.5 \times 10^{-5} \text{ S cm}^{-1}$ at 25 to 80 °C for IISERP-CON1 respectively (Figure 4.12.A and 4.12.B). However, The Nyquist plots show the proton conductivities varying from $2.90 \times 10^{-6} \text{ S cm}^{-1}$ to $6.87 \times 10^{-4} \text{ S cm}^{-1}$ at 25 to 80 °C for IISERP-COF32 respectively (Figure 4.12.C and 4.12.D). Therefore, IISERP-COF32 shows higher proton conductivity compared to IISERP-CON1.

4.2.5.2. Temperature-dependent hydrogen ion conductivity analysis of $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ and $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$

Heteroaromatic nitrogen atoms can act as protonation sites, triazole groups in IISERP-COF32 and IISERP-CON1 possess the potential to bind with proton carriers such as H_3PO_4 .^[22] To improve the proton conductivity, H_3PO_4 was successfully loaded into the channel of IISERP-COF32 and IISERP-CON1 (termed as $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ and $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$) by the method described above.^[23] Then, electrochemical impedance analyses were performed in the frequency range of 106 to 0.1 Hz with an AC amplitude of 10 mV by using a Solartron impedance analyzer. The proton conductivity of $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ and $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ were measured from room temperature 25 to 80 °C under 95% RH (relative humidity) with the pellets at similar operating conditions. The Nyquist plots shown in (Figures 4.13., 4.14., and 4.15.A) had a proton conductivity of $7.85 \times 10^{-4} \text{ S cm}^{-1}$ and $1.53 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature for H_3PO_4 loaded CON and COF, respectively, almost two orders of magnitude higher than the $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ compared to $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$.

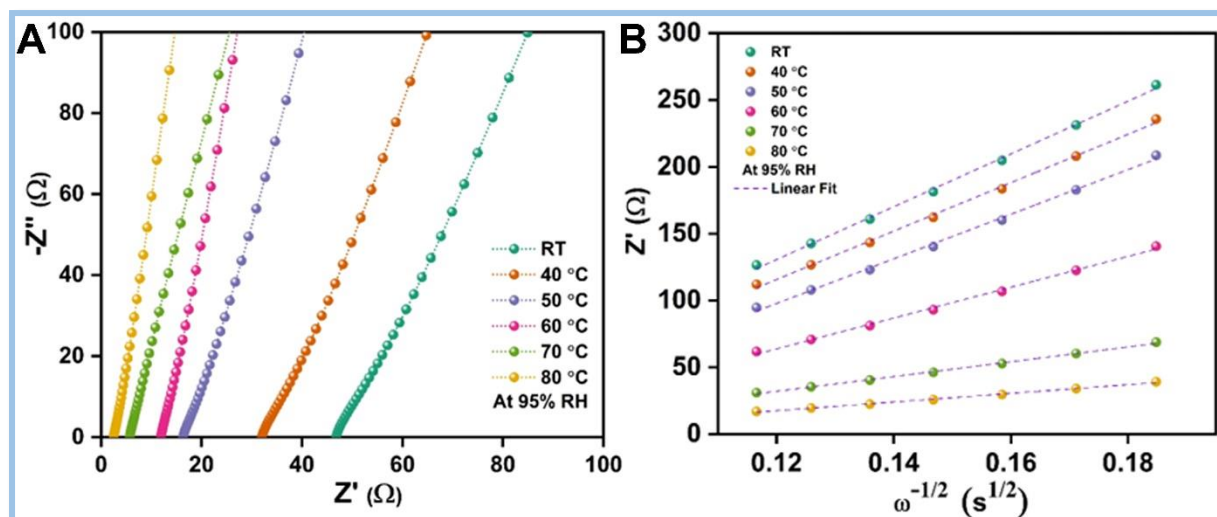


Figure 4.13. (A) Comparative Nyquist plots of $\text{H}_3\text{PO}_4\text{@IISERP-CON1}$ were measured with circular pellets under 95% RH at different temperatures. (B) A plot of the Z' versus $\omega^{-1/2}$ for $\text{H}_3\text{PO}_4\text{@IISERP-CON1}$ at 95% RH at different temperatures.

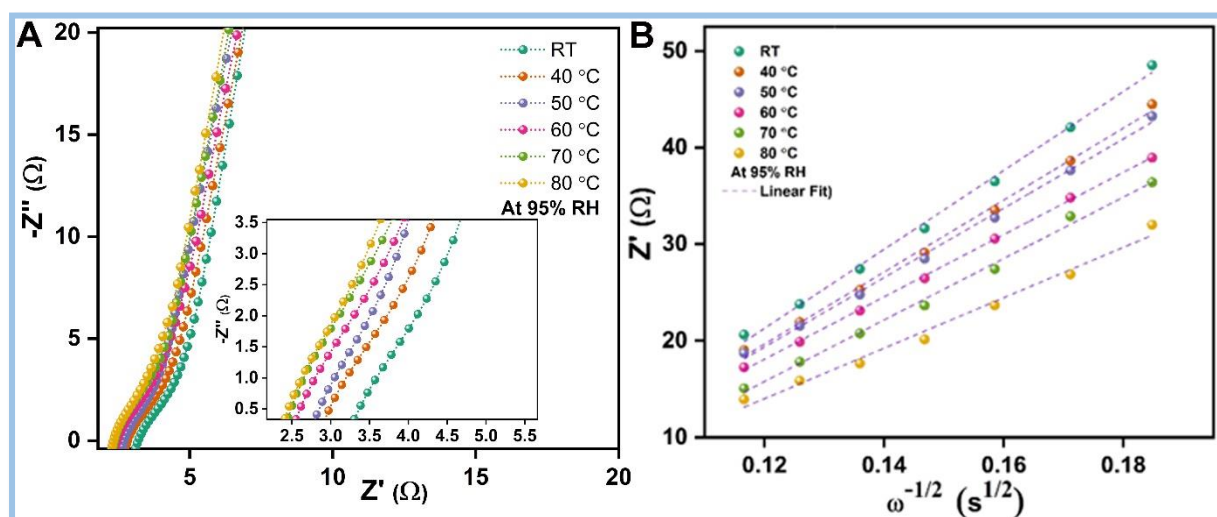


Figure 4.14. (A) Comparative Nyquist plots of $\text{H}_3\text{PO}_4\text{@IISERP-COF32}$ were measured with circular pellets under 95% RH at different temperatures. (B) A plot of the Z' versus $\omega^{-1/2}$ for $\text{H}_3\text{PO}_4\text{@IISERP-COF32}$ at 95% RH at different temperatures.

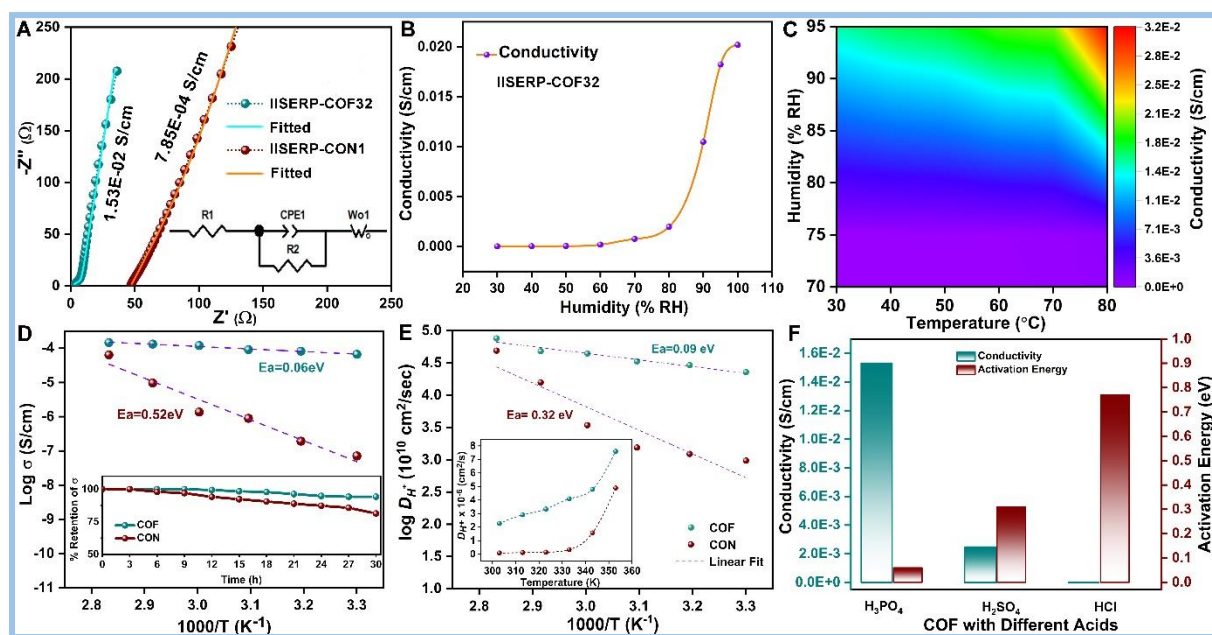


Figure 4.15. (A) Comparative Nyquist plots of $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ and $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ were measured with circular pellets under 95% RH at room temperature. (B) Conductivity at room temperature with varying humidity of $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$. (C) The density heatmap represents Conductivity at different temperatures with varying humidity of $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$. (D) Comparative Arrhenius plots of $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ and $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ for activation energies (The Inset plot represents the comparative retention of conductivity vs. time). (E) Comparative activation energies are obtained from the diffusion of protons (The Inset plot represents the comparative plot for proton diffusion coefficient at various temperatures). (F) The bar plot represents the comparative conductivities and corresponding activation energies with different acids.

With the increase in temperature, the proton conductivity value continued to rise and reached $1.51 \times 10^{-2} \text{ S cm}^{-1}$ and $3.17 \times 10^{-2} \text{ S cm}^{-1}$ at 80°C for H_3PO_4 loaded CON and COF, respectively. (Appendix Table A.3.1.). To understand the critical humidity required for high proton conductivity. The humidity-dependent proton conductivity of $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ was measured at room temperature (Figure 4.15.B). The proton conductivity value drastically increased from 10^{-4} to $10^{-2} \text{ S cm}^{-1}$ when RH raised from 30% to 95%. The activation energy (E_a) value of proton conduction for $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ was 0.06 eV calculated from temperature-dependent Arrhenius plots (Figure 4.15.D), which is remarkably low (Table 3.1).^{[17] [23] [24]} This value was much smaller than the $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ ($E_a = 0.52 \text{ eV}$) and Nafion film (0.22 eV). It suggests that $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ followed the Grotthuss mechanism ($E_a < 0.4 \text{ eV}$) and $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ followed the vehicular-type mechanism ($E_a > 0.4 \text{ eV}$).^[25] In addition, the high proton conductivity of $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ and $\text{H}_3\text{PO}_4@\text{IISERP-CON1}$ can be retained upon continuous run over 30 hours

Table 3.1. Comparison table of the best COF-based proton conducting materials.

Sr. No	Material name	σ (S/cm)	RH (%)	T (K)	Ea (eV)	References
1	PTSA@TpAzo COFM	7.80×10^{-2}	95	353	0.11	Angew. Chem. Int. Ed. 2018, 57, 10894.
2	PTSA@TpBpy COFM	6.20×10^{-2}	95	353	0.11	Angew. Chem. Int. Ed. 2018, 57, 10894
3	PTSA@TpBD(Me) ₂ COFM	5.30×10^{-2}	95	353	0.23	Angew. Chem. Int. Ed. 2018, 57, 10894
4	H ₃ PO ₄ @NKCOF-1	1.13×10^{-1}	98	353	0.14	Angew. Chem. Int. Ed. 2020, 59, 3678.
5	H ₃ PO ₄ @NKCOF-2	4.28×10^{-2}	98	353	0.24	Angew. Chem. Int. Ed. 2020, 59, 3678.
6	H ₃ PO ₄ @NKCOF-3	1.12×10^{-2}	98	353	0.40	Angew. Chem. Int. Ed. 2020, 59, 3678.
7	H ₃ PO ₄ @NKCOF-4	7.71×10^{-2}	98	353	0.08	Angew. Chem. Int. Ed. 2020, 59, 3678.
8	COF-F6-H	4.2×10^{-2}	0	413	0.09–0.5	J. Am. Chem. Soc. 2020, 142, 33, 14357–14364
9	BIP(COF)	3.20×10^{-2}	95	368	0.31	J. Am. Chem. Soc. 2019, 141, 14950
10	aza-COF-1H	1.23×10^{-3}	97	323	0.29	Chem. Meter. 2019, 31, 891.
11	aza-COF-2H	4.80×10^{-3}	97	323	0.45	Chem. Meter. 2019, 31, 891.
12	CPOS-1	1.00×10^{-2}	98	333	0.93	Angew. Chem. Int. Ed. 2018, 57, 1.
13	CPOS-2	2.20×10^{-2}	98	333	0.61	Angew. Chem. Int. Ed. 2018, 57, 1.
14	H ₃ PO ₄ @NKCOF-10	6.97×10^{-2}	90	298	0.06	Nat Commun, 2021, 12, 1982.
13	H ₃ PO ₄ @IISERP-CON1	7.85×10^{-4}	95	298	0.52	This Work
14	H ₃ PO ₄ @IISERP-CON1	1.51×10^{-2}	95	353	0.52	This Work
15	H ₃ PO ₄ @IISERP-CON32	1.53×10^{-2}	95	298	0.06	This Work
16	H ₃ PO ₄ @IISERP-COF32	3.17×10^{-2}	95	353	0.06	This Work

(Figure 4.15.D inset), suggesting that there is no leakage of H₃PO₄ and high conductivity stability in both CON and COF. Moreover, the proton conductivity IISERP-COF32 with different acids such as HCl and H₂SO₄ was measured from room temperature 25 to 80 °C under 95% RH (relative humidity) with the pellets at similar operating conditions (Figure 4.15.F). Moreover, the proton conductivity IISERP-COF32 with different acids such as HCl and H₂SO₄ was measured from room temperature 25 to 80 °C under 95% RH (relative humidity) with the pellets at similar operating conditions. The activation energies found 0.77 eV and 0.31 eV for HCl and H₂SO₄, respectively, calculated from temperature-dependent Arrhenius plots (Figures

4.15.F and A.4.5.) The water sorption, toluene sorption, CO₂ adsorption isotherms, and hydrophobic angle measurements were performed to understand the hydrophilicity and hydrophobicity properties for both CON and COF.

4.2.6. Fabrications of COF membrane and Fuel cell applications

The ultrahigh proton conductivity of H₃PO₄@IISERP-COF32 can be a promising candidate as a solid-state electrolyte in PEMFCs. COF membranes with good mechanical properties are essential for fuel cell membranes. Therefore, we fabricated a large-scale, self-standing COF-based membrane by mixing IISERP-COF32 and a small amount of HVPDF (10 wt%) (Figure 4.16.).

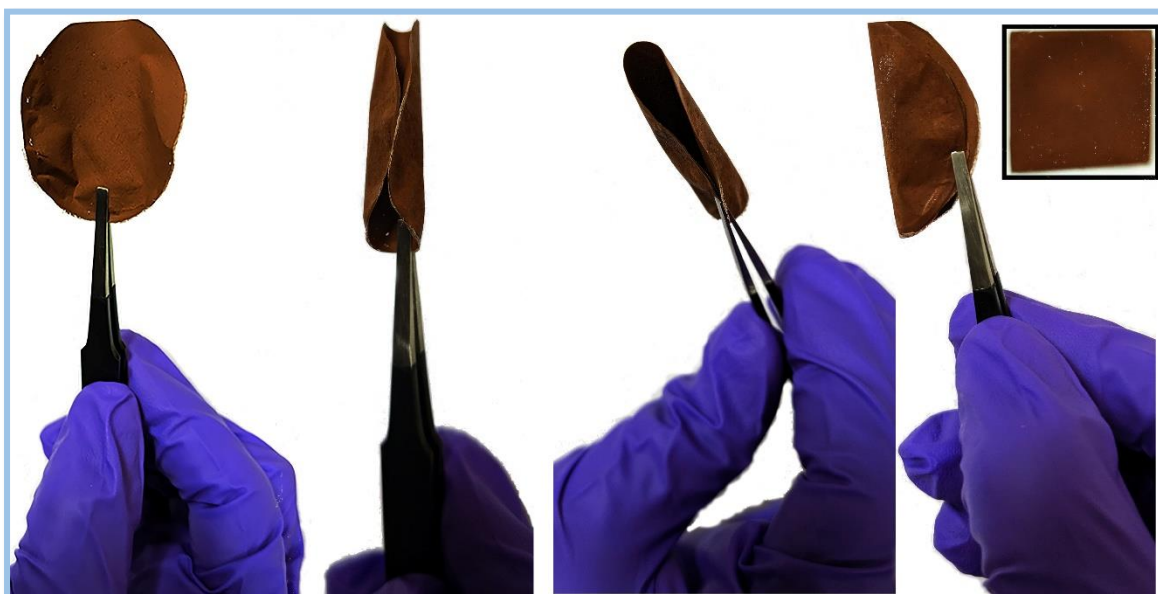


Figure 4.16. Flexible membranes at different bending modes fabricated with IISERP-COF32.

The membrane electrode assembly (MEA) was fabricated through the decal process. First, the catalyst ink was prepared with a mixture of Pt/C, Nafion, water, and isopropyl alcohol. After achieving complete dispersion of the catalysts, the ink was frozen at 5°C, resulting in a highly viscous solution mixture. The ink was then coated onto a Teflon sheet using a bar coater and dried at 120°C. The catalyst layer was transferred from the Teflon sheet to the H₃PO₄@IISERP-COF32 membrane at 120°C under a pressure of 1 ton applied by a hot press. After the successful transfer of the catalyst layer, the catalyst-coated membrane (CCM) was obtained. The MEA was created by sandwiching the gas diffusion layer (GDL) with the prepared CCM, with an active area of 2 x 2 cm², and the H₃PO₄@IISERP-COF32 membrane placed between the anode and cathode electrodes. The MEA was then placed in a single-cell test fixture (Fuel

Cell Technologies Inc, USA) measuring $2 \times 2 \text{ cm}^2$ and connected to a fuel cell test station (Fuel Cell Technologies Inc., USA). The fuel cell test employed a 40% weight percent Pt/C catalyst with a cathode loading of 0.25 mg/cm^2 , and an anode loading of 0.25 mg/cm^2 (Figure 4.17. A and A.4.6.) presents a schematic illustration of the single-cell fixture along with a magnified view of the MEA. Figure 4.17. B represents the I-V plot of the MEA assembled with $\text{H}_3\text{PO}_4\text{@IISERP-COF32}$ exhibits a maximum current density of 965 mA/cm^2 . The maximum power density calculated from the I-V plot for $\text{H}_3\text{PO}_4\text{@IISERP-COF32}$ is approximately 218 mW/cm^2 . A comparison of the current density and power density performance of the $\text{H}_3\text{PO}_4\text{@IISERP-COF32}$ -based MEA with previously reported COF-based MEAs in

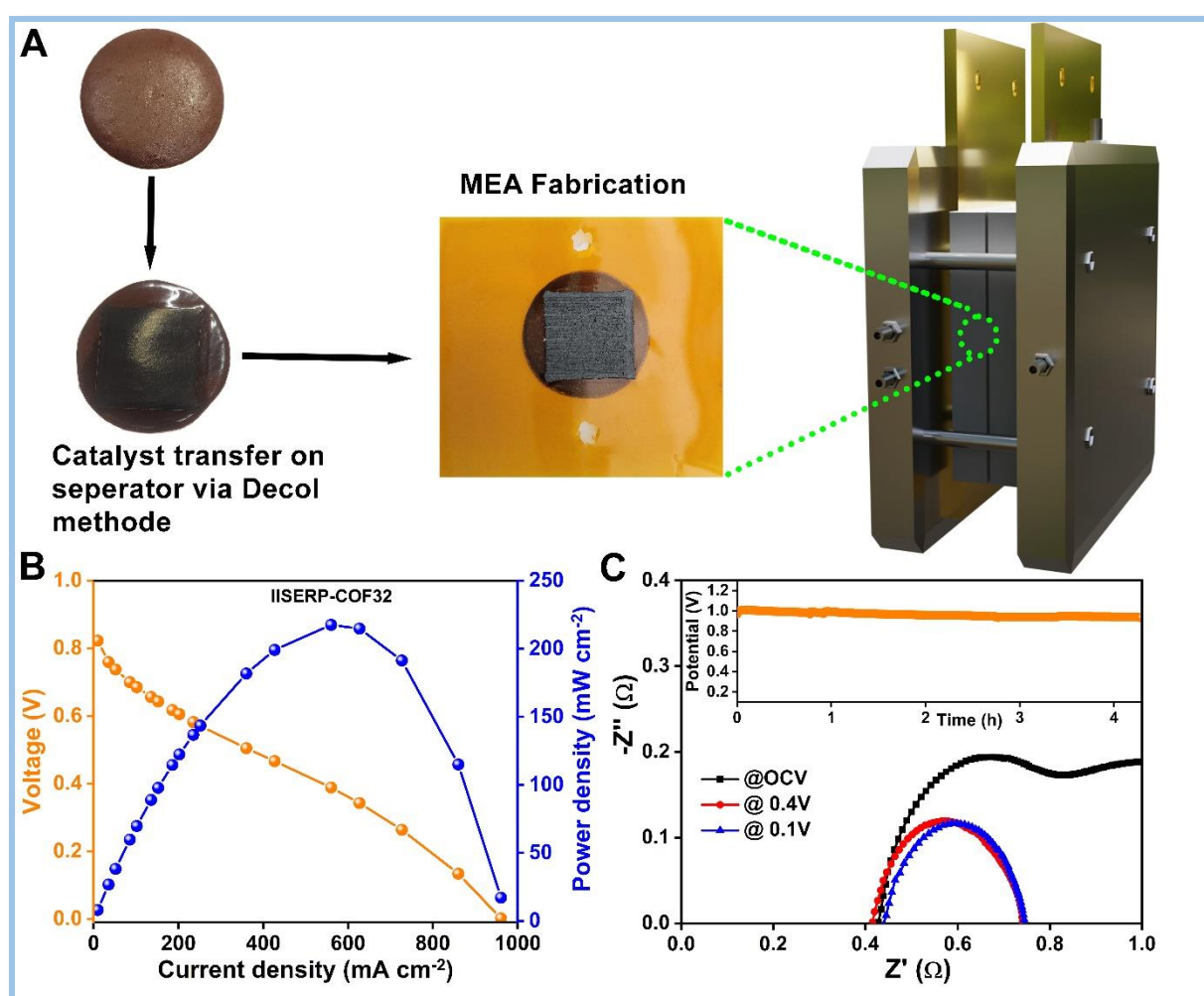


Figure 4.17. (A) The schematic diagram shown by the digital photograph of catalyst-coated IISERPCOF 32 membrane (CCM) prepared by decal method followed by hot pressed MEA and $2 \times 2 \text{ cm}^2$ fixture connected to the fuel-cell test station; (B) comparative I-V polarization plots and power density for the single-cell testing of the PEMFC using the IISERP COF-32 membrane. The testing was carried out at 35°C and 1.0 atm (H_2 and O_2) under 90% RH conditions. (C) The EIS analysis of MEA

is based on the IISERP COF-32 membrane under different operating potentials (the inset is showing the durability of the membrane at the OCV condition).

Table S4 indicates a significant improvement in performance with lower catalyst loading (0.25 mg/cm^2). The open circuit voltage (OCV) of the MEA fabricated using $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ is determined to be 0.98 V (Figure 4.17.C). The power density and current density value results reveal that the proton-conducting membrane plays a crucial role in determining its performance in actual fuel cell operation, and the consistent OCV further confirms the ability of COF membranes to prevent reactant gas crossover. Electrochemical impedance spectroscopy (EIS) measurements were conducted on the $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ -based MEA at the open circuit voltage (OCV), 0.40 V , and 0.10 V shown in Figure 4.17.C. The Nyquist plots recorded at the OCV, demonstrate that $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ exhibits higher charge transfer resistance compared to the Nyquist plots recorded at 0.40 V , indicating improved interface formation with the membrane, catalysts layer, and gas diffusion layer (GDL), thus reducing the ohmic resistance. Notably, significant changes in ohmic resistance are observed in the Nyquist plots recorded at 0.10 V . Since 0.10 V corresponds to a higher current density region with a possibility of increased water formation, the EIS spectra (Figure 4.17.C) indicate a favorable change in the ohmic resistance for the $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ based MEA. conditions. The current density and maximum power density achieved by the COF membrane were approximately 965 mA cm^{-2} and 218 mW cm^{-2} , respectively, with the lowest Pt/C loading of 0.25 mg/cm^2 by decal method. Previously, PA@TpBpy-MC COF membrane showed a maximum current density of 29 mA cm^{-2} and maximum power density of 7 mW cm^{-2} with Pt/C loading of 1 mg/cm^2 [26] and $\text{H}_3\text{PO}_4 @\text{NKCOF-1}$ based membrane showed a maximum power density of 81 mW cm^{-2} and a maximum current density of 456 mA cm^{-2} with Pt/C loading of 0.5 mg/cm^2 . [27] Recently, Zhang and co-workers reported a based membrane that achieved a maximum power of 135 mW cm^{-2} and a maximum current density of 676 mA cm^{-2} with Pt/C loading of 1 mg/cm^2 . [25] Therefore, we have the highest performance among all the COF-based membranes, with the lowest Pt/C loading reported for fuel cell applications.

4.3. Conclusion

Long-range ordering and a high degree of crystallinity of IISERP-COF32 show exceptional electrochemical ion transport properties compared to self-exfoliated IISERP-CON1 at room temperature. Our research findings provide strong evidence that the high proton conductive $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ material holds great promise for proton exchange membrane fuel cell

(PEMFC) applications. Specifically, our investigation demonstrated that an $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ membrane achieved single-cell PEMFC performance. Remarkably, the realized maximum power density and current density values of up to 218 mW/cm^2 and 965 mA/cm^2 , respectively, represent the best performance achieved for $\text{H}_3\text{PO}_4@\text{IISERP-COF32}$ materials compared to similar COF-based membranes. The proton conductivity achieved in pellets was translated to PEMFC and shows comparable performance. This ground-breaking discovery is expected to open new pathways for the environmentally friendly synthesis of innovative materials, particularly COFs, and provide valuable insights for the rational design and synthesis of polymeric materials tailored for proton exchange membrane fuel cell applications.

4.4. Acknowledgements

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4.5. References:

- [1] M. Z. Jacobson, W. G. Colella, D. M. Golden, *Science* **2005**, *308*, 1901–1905.
- [2] H. Zhang, P. Kang Shen, *Chem. Soc. Rev* **2012**, *41*, 2382–2394.
- [3] S. Shalini, V. M. Dhavale, K. M. Eldho, S. Kurungot, T. G. Ajithkumar, R. Vaidhyanathan, *Sci Rep* **2016**, *6*, 32489.
- [4] S. Shalini, T. P. Vaid, A. J. Matzger, *Chem. Comm.*, **2020**, *56*, 7245–7248.
- [5] J. A. Hurd, R. Vaidhyanathan, V. Thangadurai, C. I. Ratcliffe, I. L. Moudrakovski, G. K. H. Shimizu, *Nat. Chem.* **2009**, *1*, 705–710.
- [6] F.-M. Zhang, L.-Z. Dong, J.-S. Qin, W. Guan, J. Liu, S.-L. Li, M. Lu, Y.-Q. Lan, Z.-M. Su, H.-C. Zhou, *J. Am. Chem. Soc.* **2017**, *139*, 6183–6189.
- [7] M. K. Sarango-Ramírez, J. Park, J. Kim, Y. Yoshida, D.-W. Lim, H. Kitagawa, *Angew. Chem. Int. Ed.* **2021**, *60*, 20173–20177.
- [8] P. Ramaswamy, N. E. Wong, G. K. H. Shimizu, *Chem. Soc. Rev.* **2014**, *43*, 5913–5932.
- [9] V. R. Bakuru, M. E. DMello, S. B. Kalidindi, *ChemPhysChem* **2019**, *20*, 1177–1215.
- [10] S. Wang, M. Wahiduzzaman, L. Davis, A. Tissot, W. Shepard, J. Marrot, C. M. Corcos, D. Hamdane, G. Maurin, S. Devautour-Vinot, C. Serre. *Nat. Comm.* **2018**, *9*, 4937.

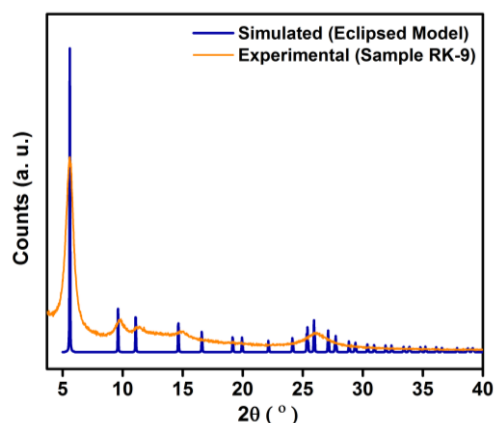
- [11] D. Mullangi, V. Dhavale, S. Shalini, S. Nandi, S. Collins, T. Woo, S. Kurungot, R. Vaidhyanathan, *Adv. Energy Mater.* **2016**, *6*, 1600110.
- [12] S. Haldar, R. Kushwaha, R. Maity, R. Vaidhyanathan, *ACS Mater. Lett.* **2019**, *1*, 490.
- [13] A. Natraj, W. Ji, J. Xin, I. Castano, D. W. Burke, A. M. Evans, M. J. Strauss, M. Ateia, L. S. Hamachi, N. C. Gianneschi, Z. A. A. Othman, J. Sun, K. Yusuf, W. R. Dichtel *J. Am. Chem. Soc.* **2022**, *144*, 43, 19813–19824.
- [14] D. Chakraborty, P. Shekhar, H. D. Singh, R. Kushwaha, C. Vinod, R. Vaidhyanathan, *Chem. - Asian J.* **2019**, *14*, 4767.
- [15] S. Haldar, K. Roy, R. Kushwaha, S. Ogale, R. Vaidhyanathan, *Adv. Energy Mater.* **2019**, *9*, 1902428.
- [16] S. Haldar, D. Rase, P. Shekhar, C. Jain, C. P. Vinod, E. Zhang, L. Shupletsov, S. Kaskel, R. Vaidhyanathan, *Adv. Energy Mater.* **2022**, *12*, 2200754.
- [17] T. Parvatkar, S. Kandambeth, A. C. Shaikh, I. Nadinov, J. Yin, V. S. Kale, G. Healing, A. H. Emwas, O. Shekhah, H. N. Alshareef, O. F. Mohammed, M. Eddaoudi *J. Am. Chem. Soc.* **2023**, *145*, 9, 5074–5082. _
- [18] R. Kushwaha, S. Haldar, P. Shekhar, A. Krishnan, J. Saha, P. Hui, C. P. Vinod, C. Subramaniam, R. Vaidhyanathan, *Adv. Energy Mater.* **2021**, *11*, 2003626.
- [19] H. Xu, S. Tao, D. Jiang, *Nature Mater.* **2016**, *15*, 722–726.
- [20] S. Haldar, K. Roy, S. Nandi, D. Chakraborty, D. Puthusseri, Y. Gawli, S. Ogale, R. Vaidhyanathan, *Adv. Energy Mater.* **2018**, *8*, 1702170.
- [21] A. Halder, S. Karak, M. Addicoat, S. Bera, A. Chakraborty, S. H. Kunjattu, P. Pachfule, T. Heine, R. Banerjee, *Angew. Chem. Int. Ed.* **2018**, *57*, 5797.
- [22] K. C. Ranjeesh, R. Illathvalappil, S. D. Veer, J. Peter, V. C. Wakchaure, K. Goudappagouda, V. Raj, S. Kurungot, S. S. Babu *J. Am. Chem. Soc.* **2019**, *141*, 38, 14950–14954.
- [23] X. Wu, Y. I. Hong, B. Xu, Y. Nishiyama, W. Jiang, J. Zhu, G. Zhang, S. Kitagawa, S. Horike, *J. Am. Chem. Soc.* **2020**, *142*, 33, 14357–14364.
- [24] Z. Meng, A. Aykanat, K. A. Mirica, *Chem. Mater.* **2019**, *31*, 3, 819–825.
- [25] Z. Wang, Y. Yang, Z. Zhao, P. Zhang, Y. Zhang, J. Liu, S. Ma, P. Cheng, Y. Chen, Z. Zhang *Nat. Comm.* **2021**, *12*, 1982.
- [26] D. B. Shinde, H. B. Aiyappa, M. Bhadra, B. P. Biswal, P. Wadge, S. Kandambeth, B. Garai, T. Kundu, S. Kurungot, R. Banerjee, *J. Mater. Chem. A* **2016**, *4*, 2682–2690.
- [27] Y. Yang, X. He, P. Zhang, Y. H. Andaloussi, H. Zhang, Z. Jiang, Y. Chen, S. Ma, P. Cheng, Z. Zhang *Angew. Chem. Int. Ed.* **2020**, *59*, 3678–3684.

Table A.2.1. IR data peak assignments.

COF-Name	Enolic OH (cm ⁻¹)	carbonyl (C=O) (cm ⁻¹)	C=N bond (cm ⁻¹)	C=N aromatic (cm ⁻¹)	C=C bond (cm ⁻¹)	C-N bond (cm ⁻¹)
IISERP-COF25	3390	1675	1620	1565	1480	1320

Structure modelling and characterizations of the COFs:

A structure consistent with the experimentally observed powder pattern was obtained using a combination of crystal building simulations, Pawley refinements and Density Functional Theory (DFT) based geometry-optimizations carried out using the Accelrys program (Materials Studio V.6.0).

**Figure A.2.1.** A comparison of the reflections from the simulated PXRD pattern of the eclipsed configuration with the experimental PXRD pattern.

Atomic-modeling and geometry-optimization using DFT (CASTEP): In brief, the powder XRD was indexed using an X-Cell program. Following this, a space group search was executed, which suggested P6/m and P-6 as the probable ones (high figure of merit values (> 120)). A crystal building was carried out in the P6/m setting, however, the introduction of the –OH moiety of the phenolic group in the aldehyde building unit lowers the symmetry to triclinic, P1. A comparison of the experimental powder X-ray diffraction with the simulated XRD patterns of the eclipsed, staggered, and slipped layer configurations revealed the reflections from the eclipsed configuration matching well both in peak positions and relative intensity with the experimental PXRD (Figure S1 and S2). The structures of the eclipsed form were geometry optimized using the CASTEP routine embedded in the Materials Studio ("First principles methods using CASTEP" Zeitschrift fuer Kristallographie, **2005**, 220(5-6) pp. 567-570). The lowest energy configuration was that of the eclipsed structure (Total energy: -6996 eV, Figure S3). It has lower relative energy compared to the staggered form as well as the slipped form. Importantly, the pore sizes estimated for the eclipsed model fit the experimentally determined pore sizes

much better. Hence, the eclipsed configuration with an AAA... stacking was used as the better-fitting model.

Pawley refinements: Pawley refinements were carried out using the eclipsed model in the P1 space group. An excellent fit was obtained ($R_p = 4.1\%$; $wR_p = 7.3\%$). The reflections from the experimental pattern could be indexed well to this P1 model, which is only a slight deviation from the higher symmetry P6/m model (Table S1). The Pawley fit with the indexed reflections is shown in Figure 1 of the main text.

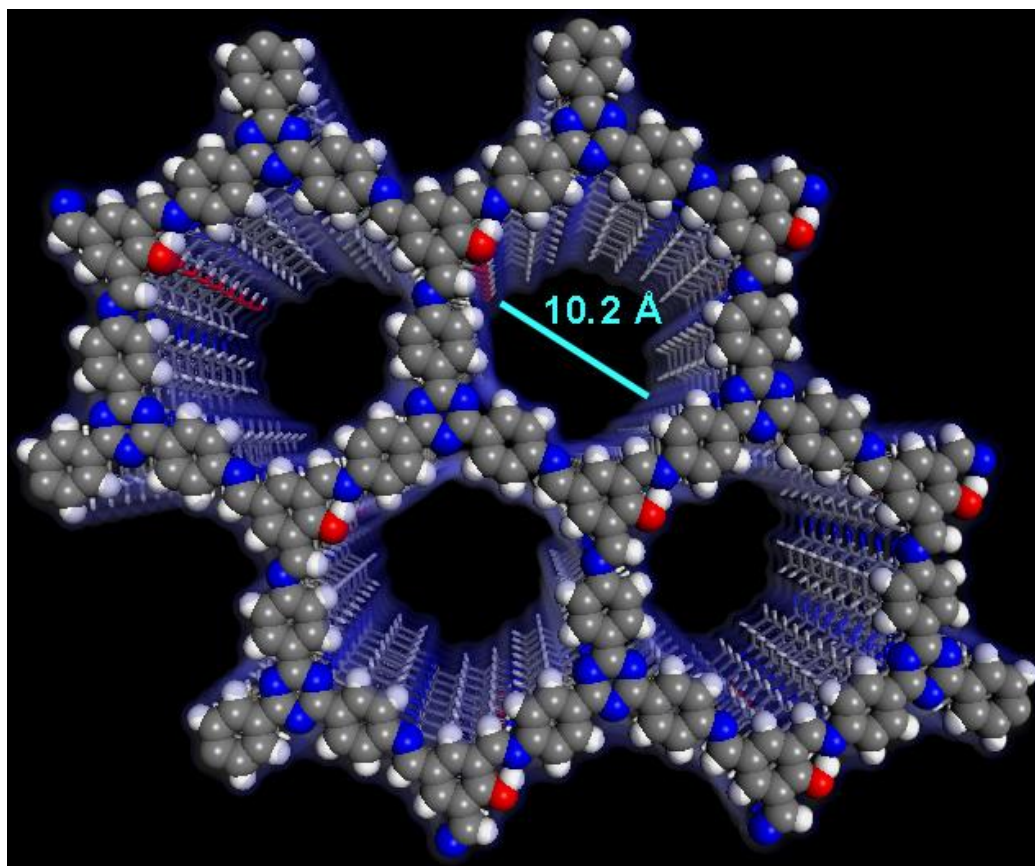


Figure A.2.2. The Pawley refined structure of the IISERP-COF25 showing the uniform 1-D channels formed by the AAA... layer stacking of the eclipsed configuration.

Table A.2.2. Atomic coordinates of IISERP-COF25. Structure refined from Pawley methods.

Space group: P1

Lattice: Parameters $a = 18.6397$ $b = 18.6416$ $c = 3.5307$ $\alpha = 90$ $\beta = 90$ $\gamma = 120.0338$

Atom	X	Y	Z	Occupancy
C1	0.26753	0.49017	0.54626	1
N2	0.19013	0.43593	0.48529	1

C3	0.64954	0.80752	0.53834	1
C4	0.27897	0.70063	0.51984	1
C5	0.36503	0.75405	0.5264	1
C6	0.20395	0.30845	0.46424	1
C7	0.1651	0.22257	0.45813	1
C8	0.07823	0.17316	0.46825	1
C9	0.03211	0.21381	0.48538	1
C10	0.07086	0.29943	0.49651	1
C11	0.0363	0.08157	0.4657	1
N12	0.0838	0.04592	0.4561	1
C13	0.50805	0.77975	0.53443	1
N14	0.56248	0.75482	0.54144	1
C15	0.19176	0.84323	0.47695	1
C16	0.29948	0.5799	0.53763	1
C17	0.24798	0.61465	0.52485	1
C18	0.69089	0.89477	0.53905	1
C19	0.77674	0.94215	0.52907	1
C20	0.82551	0.90439	0.51729	1
C21	0.78455	0.81747	0.52458	1
C22	0.69863	0.76987	0.53362	1
C23	0.9174	0.95478	0.49245	1
N24	0.95249	0.03786	0.48028	1
C25	0.22125	0.73222	0.50137	1
N26	0.2459	0.81094	0.49489	1
C27	0.15778	0.34944	0.48588	1
C28	0.41938	0.72286	0.5364	1
C29	0.38678	0.63477	0.54562	1

C30	0.10441	0.7964	0.46566	1
C31	0.05682	0.83446	0.45967	1
C32	0.09399	0.92128	0.46226	1
C33	0.18089	0.96821	0.46672	1
C34	0.22837	0.93017	0.47372	1
C35	0.04368	0.9622	0.46541	1
N36	0.96017	0.91408	0.48394	1
O37	0.4398	0.60625	0.55929	1

Thermal stability:

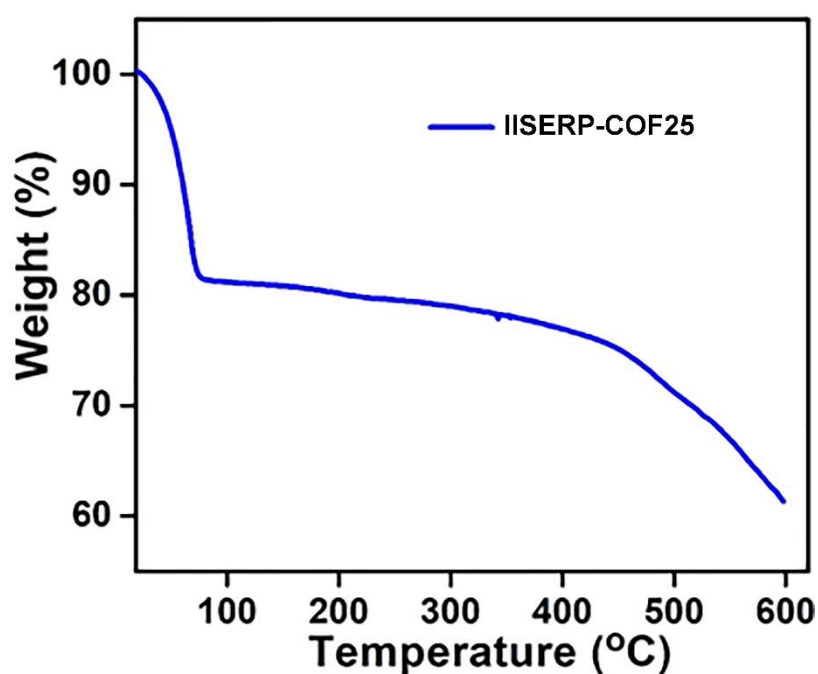


Figure A.2.3. Thermogravimetric analysis of the COF under N₂ flow at 5K/min rate.

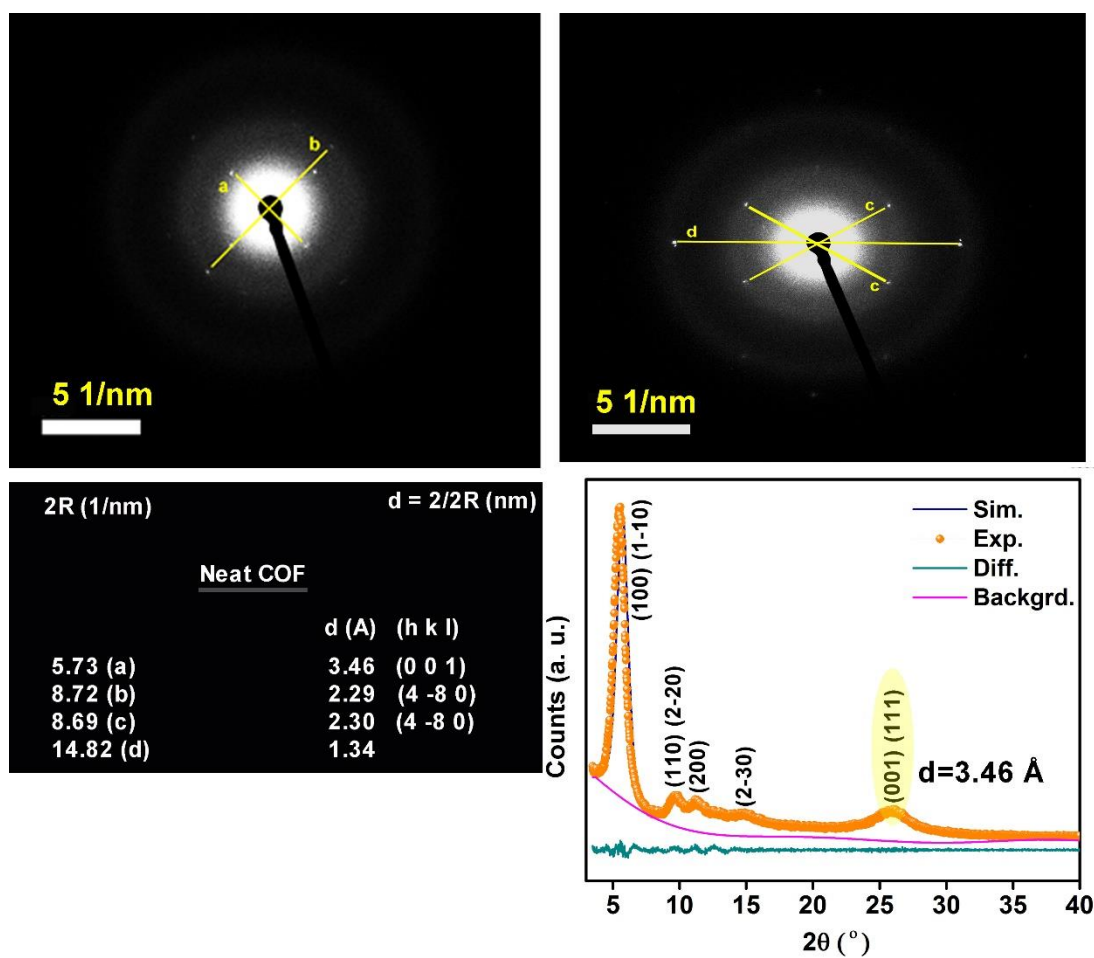


Figure A.2.4. Top: The SAED pattern of the as-synthesized IISERP-COF25 showing the diffraction spots from different planes. Some of them correspond to the reflections from the PXRD.

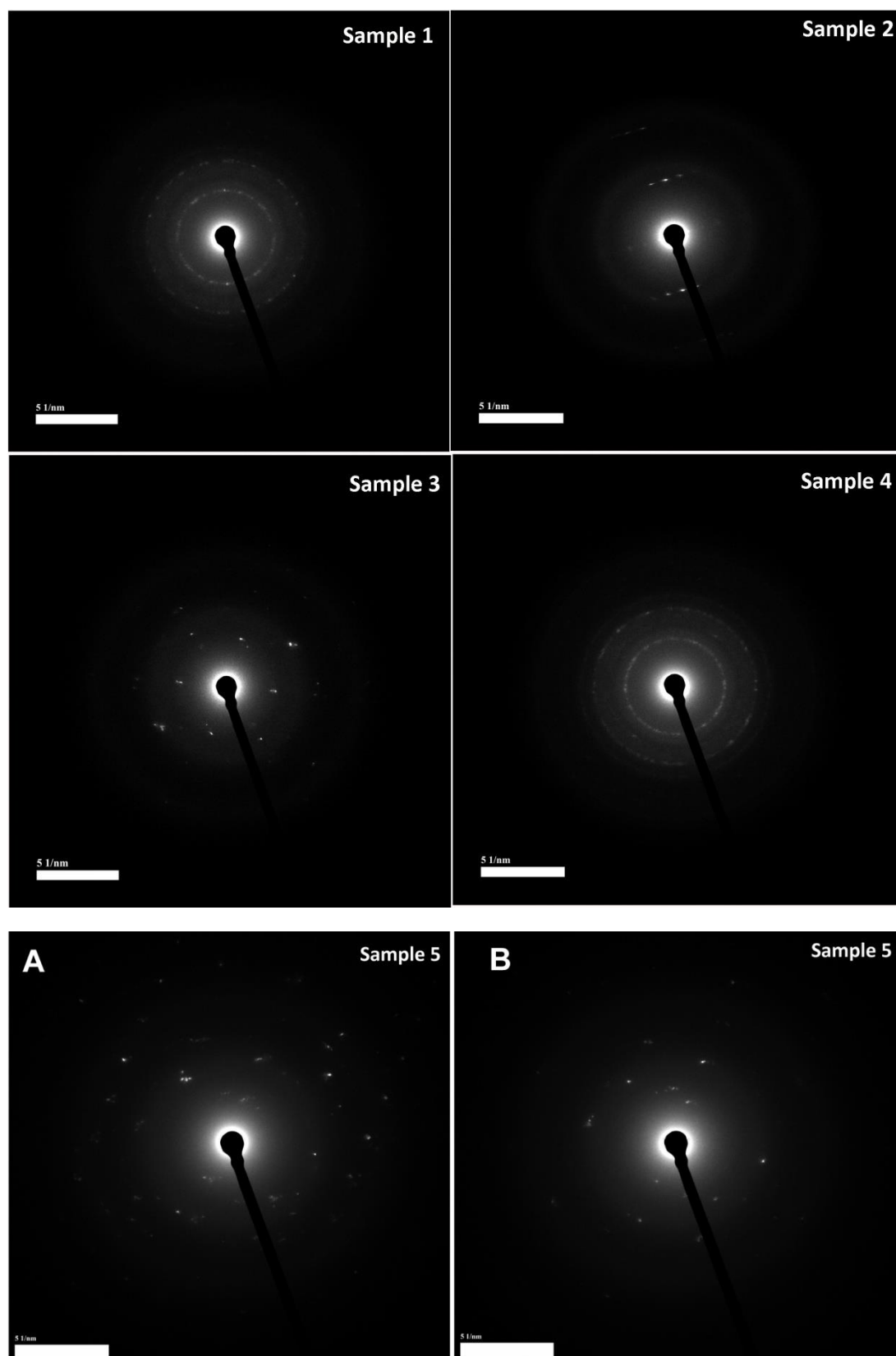


Figure A.2.5. SAED images from multiple sample preparations of IISERP-COF25. Consistent polycrystallinity could be observed.

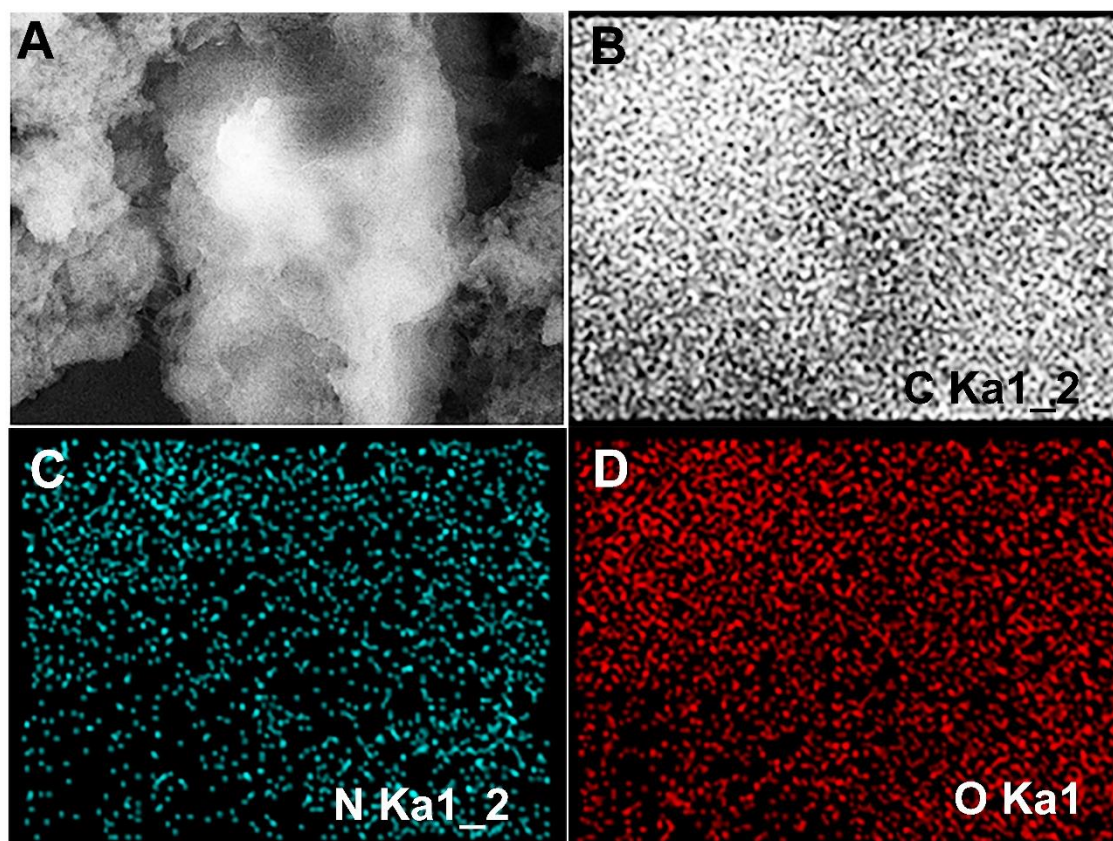


Figure A.2.6. The elemental mapping reveals the homogeneous distribution of constituents in the as-made COF.

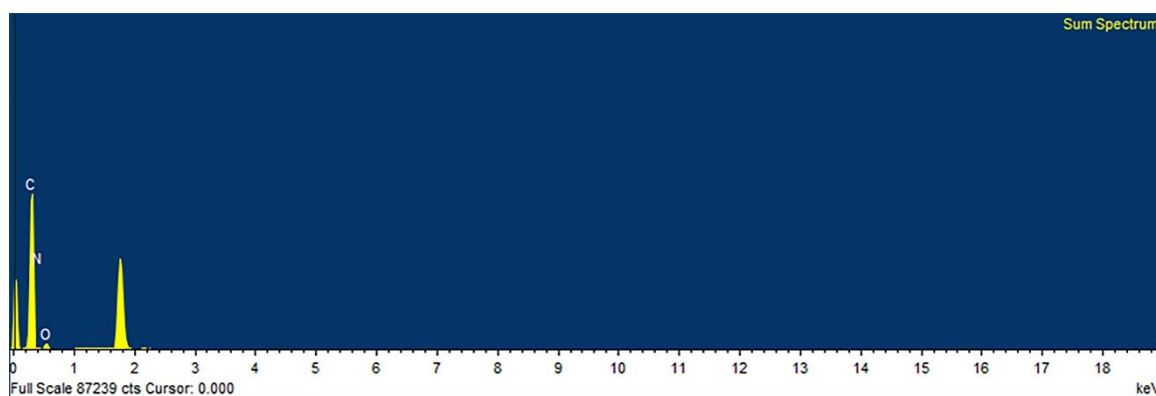


Figure A.2.7. The EDAX assisted full-scale spectrum of as-made COF shows the elements present in the sample.

4. Electrochemical measurements

The redox activity of the IISERP-COF25 seen from CV measurements in nonaqueous medium:

An electrode was fabricated by coating an ethanolic slurry of the COF on Toray carbon paper. Then it was dried in vacuum for 12 hrs. The CV measurements were performed in a non-aqueous electrolyte (t-butyl ammonium hexafluorophosphate dissolved in acetonitrile) using the three-electrode system. A non-aqueous Ag/AgNO₃ reference electrode and Toray paper counter electrodes were used. CV measurements were carried in a 2 mV/s scan rate within the potential window from -0.5 to -3 V.

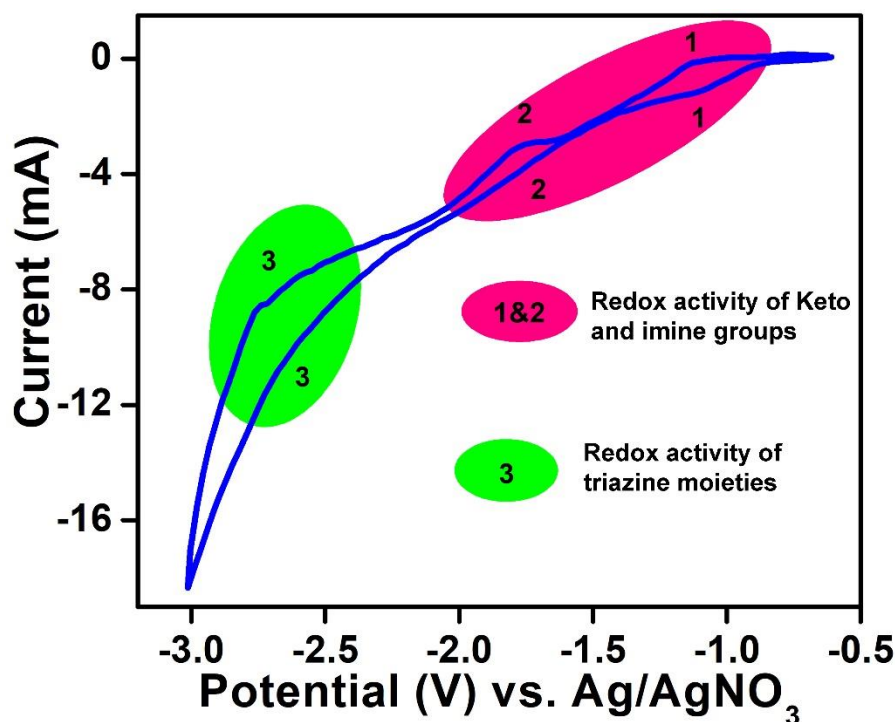


Figure A.2.8. Cyclic voltammetry measurements of IISERP-COF25 @2 mV/s using 0.5 (M) solution of nonaqueous electrolyte (t-butyl ammonium hexafluorophosphate dissolved in acetonitrile).

Capacitance estimation three-electrode setup

The specific capacitance (C_{sp}) of the active electrode material was determined from the equation

The integral equation below. A detailed derivation of the equation can be seen (*Nat. Commun.* **2013**, 4, 2923., *Sci Rep* **2016**, 6, 25793., *Adv. Energy Mater* **2020**, 10, 2001673., *J. Mater. Chem. A*, **2013**, 1, 1086-1095.).

$$C_{sp} = 2 \cdot I_m \cdot \frac{\int(V \cdot dt)}{(\Delta V)^2} \dots \dots \dots \text{Eq A.2.1 (using Non-linear GCD curve)}$$

where C_{sp} is the specific capacitance (F/g) sample Where I_m = current density in A/g, calculated from the coated samples' mass, $\int(V \cdot dt)$ = integral area of the discharging part of the GCD curve, ΔV = Potential window ($V = V_f - V_i$), and considering IR drop.

Cyclic Voltammetry measurements in 1 M H₂SO₄ electrolyte solution:

For electrochemical measurements, a glassy carbon electrode was employed as the working

electrode. Ag/AgCl and Platinum were used as the reference and the counter electrodes, respectively. The working electrode was coated with active materials (COF). At first, the glassy carbon electrode was polished to a mirror-finish by using 0.05-micron alumina powder, thoroughly cleaned by sonicating in water for 15 min, and dried in air. Thereafter, in about 1 mL ethanol, COF (8 mg; 80%), Super P carbon (1.5 mg; 15%) and Nafion binder (0.5 mg; 15%) were added. The solution was sonicated for 10 hr to make the solution homogeneous. In the next step, 5 μ l of the solution was drop-casted on the glassy carbon electrode.

Finally, the electrode was dried in a hot air oven for 20 min. The CV measurements were performed using 1 M H_2SO_4 as the electrolyte using a typical three-electrode set-up. The scan rates were varied from 5 to 1000 mV/s within a potential window of 0-0.8 V (Figure S21).

Note: These three-electrode measurements using relatively smaller amounts of samples on a glassy carbon electrode has been done for mechanistic understanding.

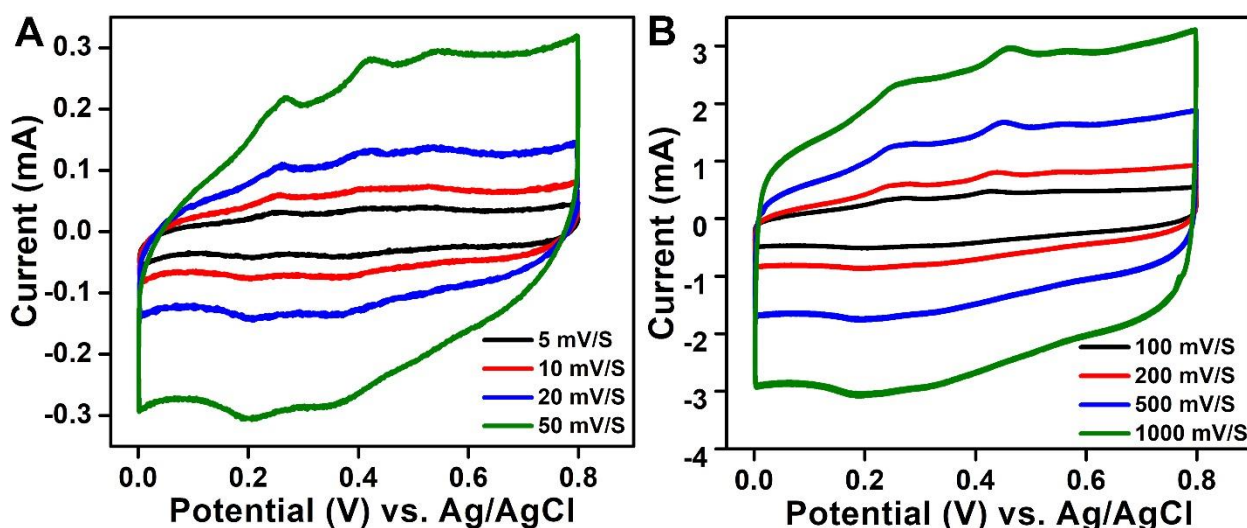


Figure A.2.9. CV measurements of the COF-coated working electrode at variable scan rates in 1 M H_2SO_4 electrolyte solution with 0.04 mg loading of active material. (A) from 5 to 50 mV/s and (B) from 100 to 1000 mV/s within the potential window of 0-0.8 V. All three redox peaks appeared even at fast scan rates.

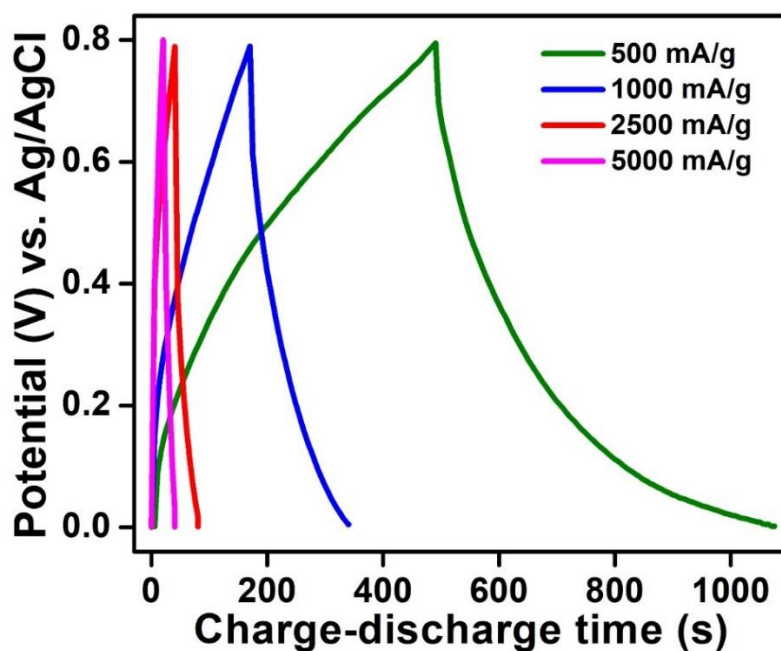


Figure A.2.10. Galvanostatic charge-discharge curves for the COF at varying current densities (from 500 mA/g to 5000 mA/g) in 1 M H_2SO_4 electrolyte solution from a three-electrode configuration.

Cyclic Voltammetry measurements in 1 M H_2SO_4 + 0.2 M KI electrolyte solution for the Composite electrode (COF + Carbon + Nafion Binder):

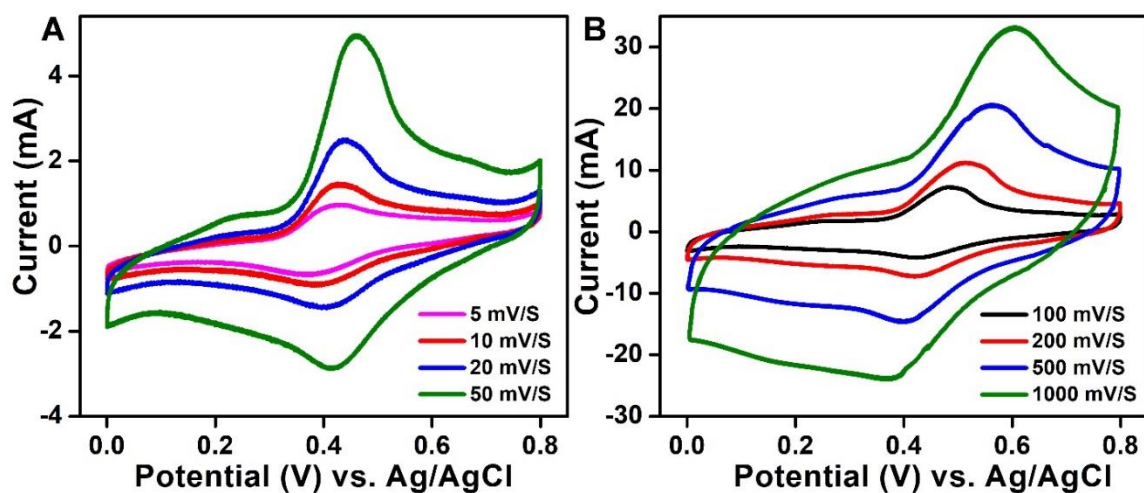


Figure A.2.11. Three-electrode CV measurements of the COF-coated working electrode at variable scan rates in 1 M H_2SO_4 + 0.2 M KI electrolyte solution (A) from 5 to 50 mV/s and (B) from 100 to 1000 mV/s within the potential window of 0 - 0.8 V.

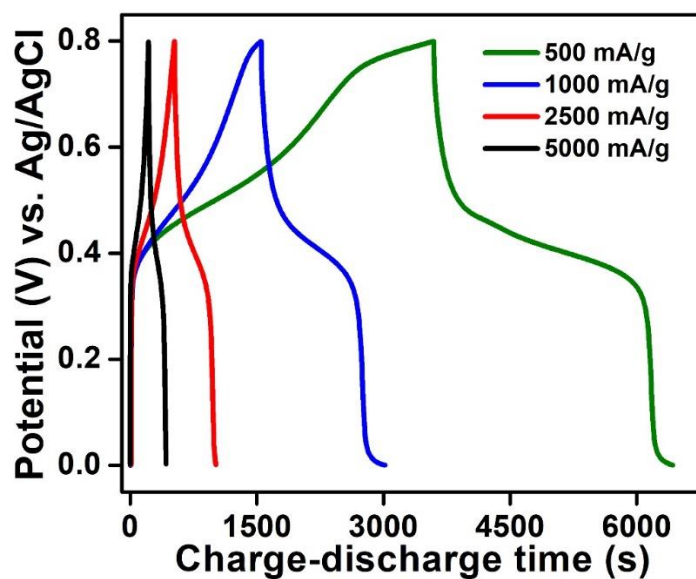


Figure A.2.12. Galvanostatic charge-discharge curves for the COF-coated at varying current densities (from 500 mA/g to 5000 mA/g measured in 1 M H_2SO_4 + 0.2 M KI electrolyte solution in a three-electrode assembly).

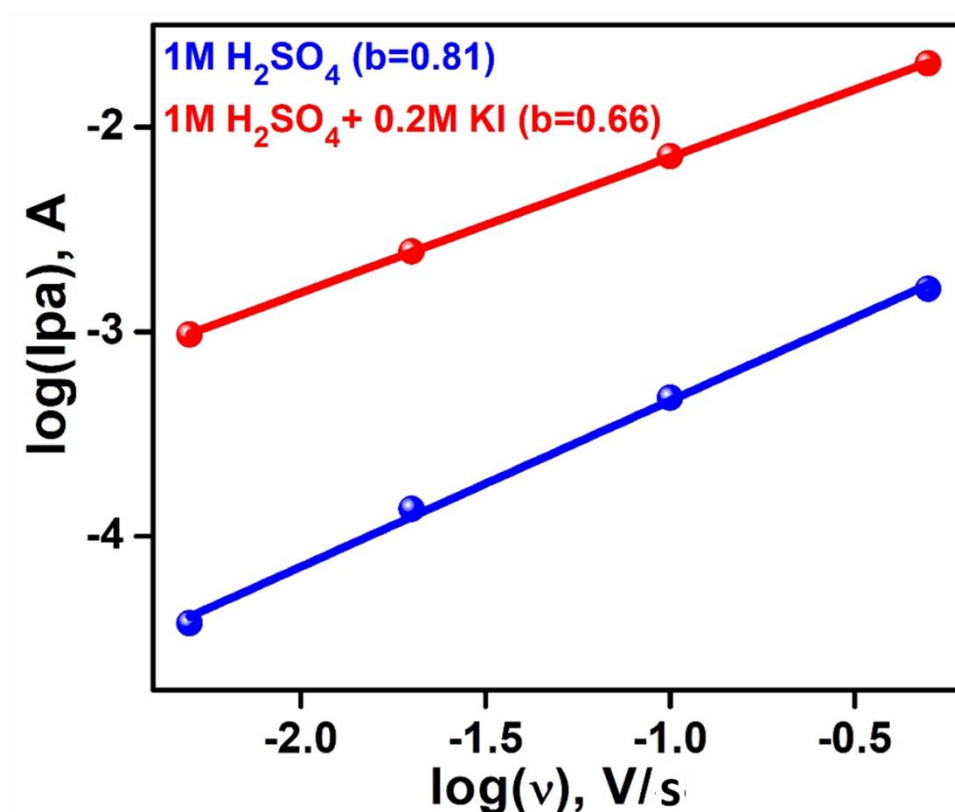


Figure A.2.13. A plot of the $\log(I_{pa})$ vs. $\log(v)$ measured in acid vs. redox electrolyte. Where I_{pa} is anodic peak current and v is scan rate employed for the cyclic voltammograms measured in three-electrode assembly using composite-coated glassy carbon as the working electrode.

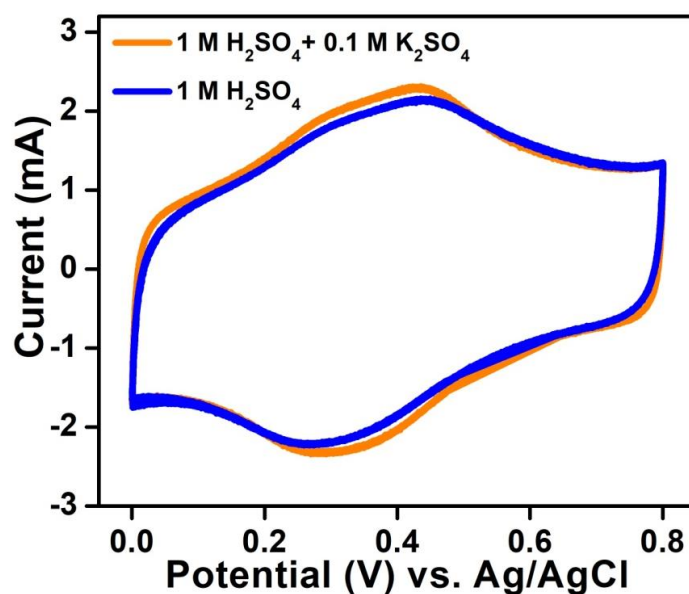


Figure A.2.14. Comparative CV plots of the composite-electrode (15% Super P carbon + 80% IISERP-COF25 + 5% Nafion binder) measured using 1 M H₂SO₄ and 1 M H₂SO₄ + 0.1 M K₂SO₄ as electrolyte. Note: We have maintained the number of moles of K⁺ present in redox electrolyte (1 M H₂SO₄ + 0.2 M KI).

Surface vs redox storage:

For better understanding, the surface and redox components of the overall capacitance in the three-electrode system with KI + H₂SO₄ electrolyte have been calculated. It shows the enhancement in overall capacitance with the enhancement of pseudocapacitance for the latter. The quantification of the Faradaic component and surface one is done using the following equation, and a graphical representation is provided for better understanding (equation 2, Figure S26). It shows that even at very high scan rates, there is a significant amount of differences in the pseudocapacitance contribution for the KI + H₂SO₄ electrolyte at different scan rates.

Equation:

$$I = k_1v + k_2v^{0.5} \dots\dots\dots \text{Eq A.2.2.}$$

Where I is the maximum current obtained at the fixed scan rate, v is the scan rate, k_1 , and k_2 are constants. The value of k_1 and k_2 have been obtained by using two different equations at two different scan rates.

$$i = i_1 + i_2$$

Where, $i_1 = k_1v$ (corresponds to pure electrostatic surface storage) and $i_2 = k_2v^{0.5}$ (corresponds to pure pseudo behavior)

$$\text{Where, } i = k_1v + k_2v^{0.5}$$

In this equation, i is the maximum peak current obtained at a certain scan rate v , and k_1 and k_2 are arbitrary constants.

The value of these two arbitrary constants k_1 and k_2 can be calculated by solving the below two equations comes from $i = k_1v + k_2v^{0.5}$ using two different scan rates ($v_{(a)}$ and $v_{(b)}$).

$$i_{(a)} = k_1v_{(a)} + k_2v_{(a)}^{0.5}$$

$$i_{(b)} = k_1v_{(b)} + k_2v_{(b)}^{0.5}$$

For the calculation we have kept $i_{(a)} = k_1v_{(a)} + k_2v_{(a)}^{0.5}$ fixed, where $v_{(a)} = 2$ mV/s and varied the $i_{(b)} = k_1v_{(b)} + k_2v_{(b)}^{0.5}$ where $v_{(b)} = 5$ mV/s, 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s, 250 mV/s, 500 mV/s, 1000 mV/s.

We have used the k_1 and k_2 values obtained from the above calculations to calculate the contribution of surface and redox storage at different scan rates.

$$\text{Contribution from surface (in \%)} = [i_1/(i_1+i_2)] \times 100$$

$$\text{Contribution from redox (in \%)} = [100 - \text{surface}]$$

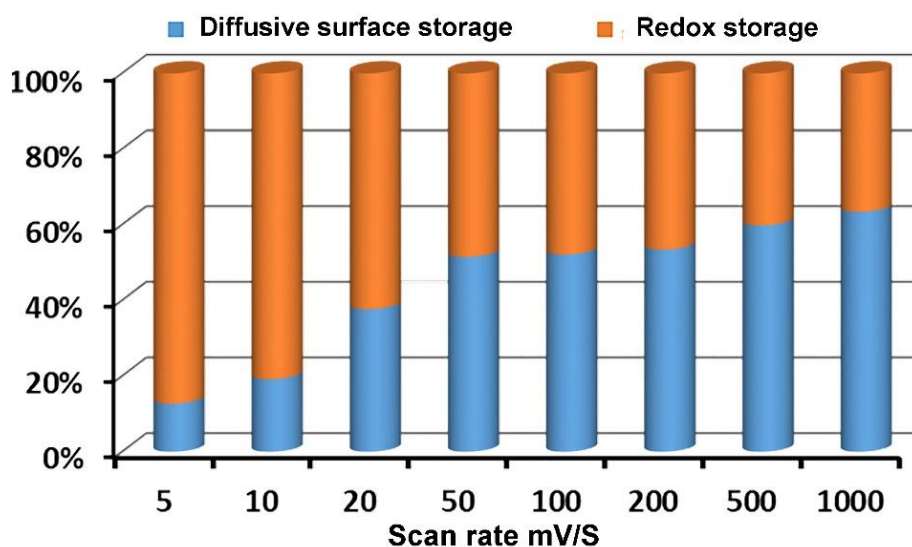


Figure A.2.15. A bar chart representation of the contribution of surface storage and storage by redox active sites of the composite-electrode at various scan rates in CV using 1 M H_2SO_4 + 0.2 M KI as an electrolyte.

Capacitance calculation with higher mass loadings on Toray carbon paper:

The COF (16 mg; 80%), Super P carbon (3 mg; 15%) were mixed in a mortar-pestle. It was ground thoroughly to make a homogeneous mixture, to which the Nafion solution (1 mg; 15%), and 2 mL ethanol were added and ground into a homogenous slurry. This slurry was kept at 60 °C to evaporate the ethanol. Then the composite material was reground. The fine-powered composite material of 2.00 mg was measured using a balance (Sartorius Quintix35-1S semi microbalance) with a precision of 0.01 mg. Contents were dispersed in 0.5 mL ethanol in an Eppendorf and sonicated for 2 hrs. It was drop-casted on a 1cm x 1cm area of the Toray paper of size 1cm x 4cm and dried. The excess area of the Toray paper was covered with scotch tape so that only the coated area would be exposed to the solution. Ag/AgCl and large Platinum flag were used as the reference and the counter electrodes. A potential

window of 0.1 to 0.8 V was employed to avoid the interference from hydrogen evolution at potentials below 0.1 V. Moreover, we prepared three batches of samples for estimating the experimental error in the capacitance calculations, which was calculated using the integral eq 1.

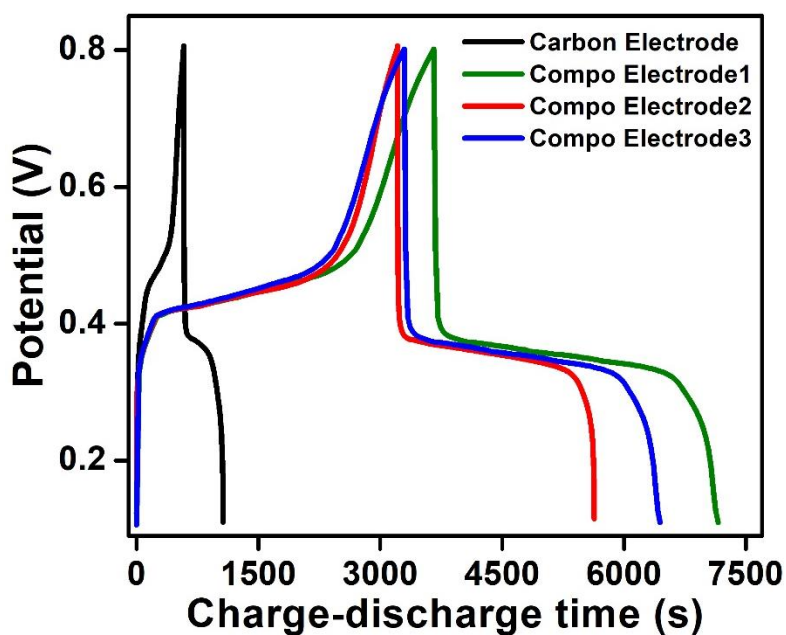


Figure A.2.16. A comparative plot of charge-discharge measurements done using the redox electrolyte (1 M H_2SO_4 + 0.2 M KI) on three different sets of electrodes. The amount of charge stored was found to be 1469.01 ± 127.87 C/g.

Table A.2.3. Comparison of the specific capacitance of COF and COF-derived electrode materials in three-electrode set-up.

Electrode materials	Electrolytes	Working Voltage (V) (vs reference electrode)	Current density (A/g)	Specific capacitance (F/g)	Charge Q (C/g)	References
TPDA-1	1 M H ₂ SO ₄	0 to 1 (vs SCE)	0.5	348	348	A.2.1. ^a
TFP-NDA-COF	1 M H ₂ SO ₄	0 to 1 (vs SCE)	0.5	348	348	A.2.2 ^a
TpPa-(OH) ₂	1 M phosphate buffer	-0.2 to 0.5 (vs SCE)	0.5	416	291.2	A.2.3 ^a
TAPT-DHTA-COF0.1@PP	6 M KOH	-1 to 0 (vs Ag/AgCl)	0.5	411	411	A.2.4 ^a
TpPa-COF-SWCNTs	1 M H ₂ SO ₄	-0.2 to 0.75 (vs SCE)	0.5	153	145.35	A.2.5 ^a
carbonized ACOF1	6 M KOH	-1 to 0 (vs Ag/AgCl)	1	234	234	A.2.6 ^a
carbonized COF1	6 M KOH	-1 to 0 (vs Ag/AgCl)	1	191	191	A.2.6 ^a
COFs/NH ₂ -Rgo	1 M Na ₂ SO ₄	0 to 0.5 (vs SCE)	0.2	533	266.5	A.2.7 ^a
Hex-Aza-COF-2	1 M H ₂ SO ₄	-1 to 0 (vs Hg-Hg ₂ SO ₄)	1	585	585	A.2.8 ^c
Hex-Aza-COF-3	1 M H ₂ SO ₄	-1.1 to 0.1 (vs Hg-Hg ₂ SO ₄)	1	663	795.6	A.2.8 ^c
Hex-Aza-COF-1	1 M H ₂ SO ₄	-1 to 0 (vs Hg-Hg ₂ SO ₄)	1	220	220	A.2.8 ^c
IISERP-COF10	1 M H ₂ SO ₄	0 to 0.8 (vs Ag/AgCl)	0.5	546	436.8	A.2.9 ^c
PEDOT@AQ-COF	1 M H ₂ SO ₄	-0.2 to 0.6 (vs Ag/AgCl)	1	1663	1330.4	A.2.10 ^a
IISERP-COF25	1 M H ₂ SO ₄ 1 M H ₂ SO ₄ + 0.2 M KI	0.1 to 0.8 (vs Ag/AgCl)	0.5 0.5	290.27±32.65 2,098.59±182.68	203.19±22.86 1469.01±127.87	This Work

Type of measurement set-up used in these studies: a = three-electrode set-up only, b = two-electrode device only and c = both (two and three-electrode set-up)

Impedance analysis of the composite and neat COF using three-electrode setup:

Impedance analysis was performed for the composite and neat COF by coating them on the Toray paper (1cm x 1cm) area was employed as the working electrode. Ag/AgCl and large Platinum Flag were used

as the reference and the counter electrodes. The frequencies were varied from 1 MHz to 10 mHz at a constant open-circuit potential with a scan rate of 5 mV/s.

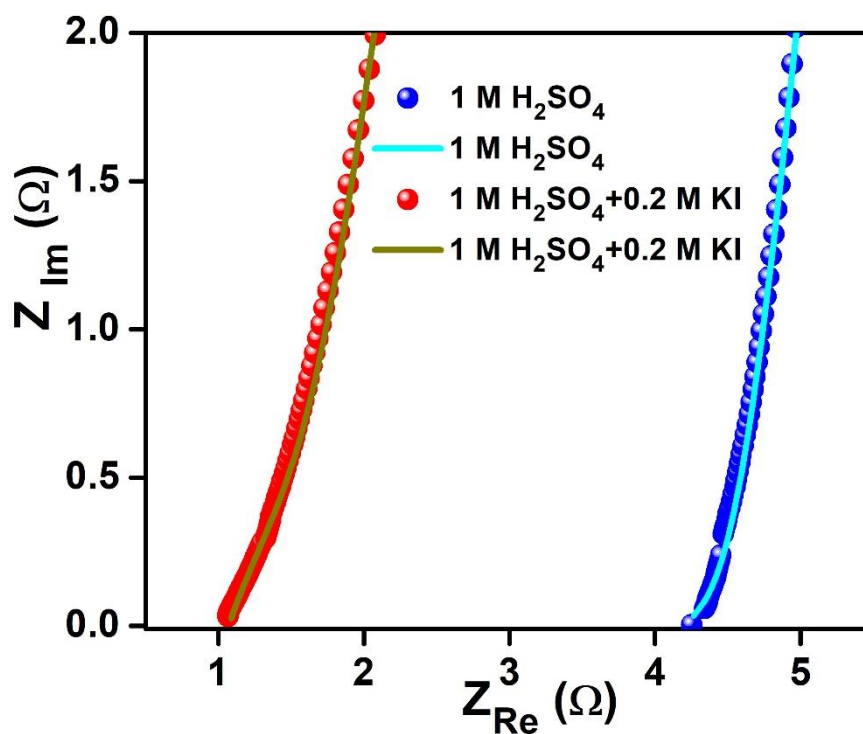


Figure A.2.17. Zoomed Nyquist plots from the AC-impedance measurements of the composite in the three-electrode assembly in 1 M H₂SO₄ and 1 M H₂SO₄ + 0.2M KI electrolyte system.

Table A.2.4. Comparison of circuit elements of composite with H₂SO₄ and H₂SO₄ + KI in three-electrode setup.

Circuit elements	Composite (H ₂ SO ₄)	Composite (H ₂ SO ₄ + KI)
Rs (ohm)	4.447	1.06
Rct (ohm)	0.789	0.2432
Q1	0.06976	0.005359
n1	0.778	0.7711
Wo	0.416	0.1038
Q2	0.02178	0.02034
n2	0.9392	0.9723
χ ²	2.665E-4	0.0002606
Meas. error	< 1.633 pct.	< 1.614 pct.

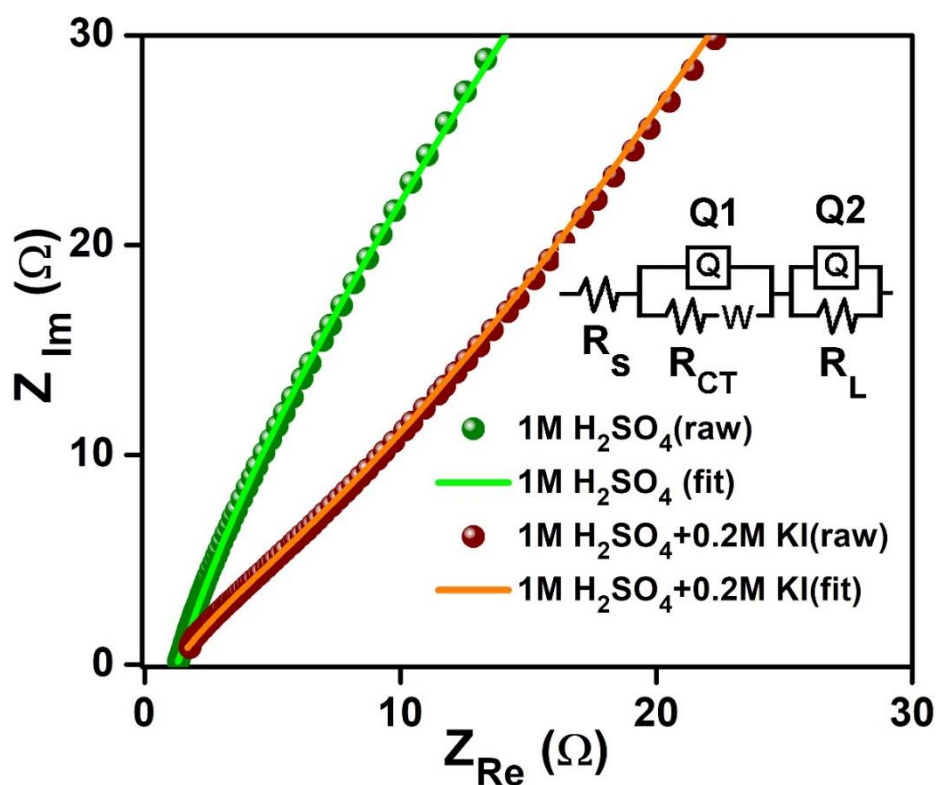


Figure A.2.18. Nyquist plots from the AC-impedance measurements of the neat COF in the three-electrode assembly in 1M H_2SO_4 and 1M H_2SO_4 + 0.2M KI electrolyte system.

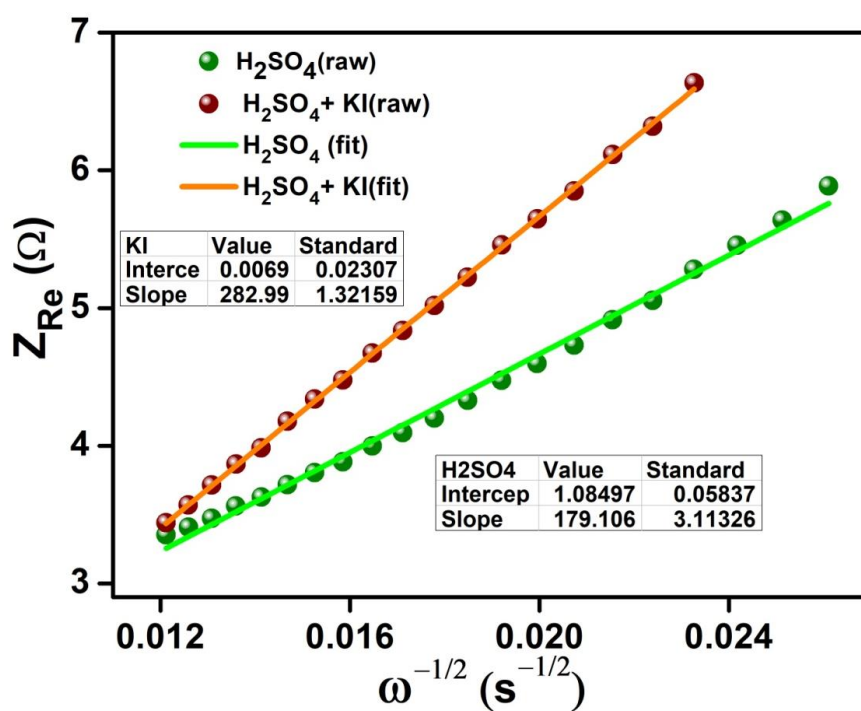


Figure A.2.19. A plot of the Z_{Re} vs. Inverse square root of frequency (ω) of COF in 1 M H_2SO_4 and 1 M H_2SO_4 + 0.2M KI electrolyte. The slope of the linear fit reflects the diffusion kinetics.

Table A.2.5. Comparison of circuit elements of neat COF with H₂SO₄ and H₂SO₄ + KI in three-electrode setup.

Circuit elements	Neat COF (H ₂ SO ₄)	Neat COF (H ₂ SO ₄ + KI)
Rs (ohm)	2.395	1.142
Rct (ohm)	2.01	0.7513
Q1	0.0001881	0.000112
n1	0.8335	0.8818
Wo	0.00008379	0.000487
Q2	0.00363	0.0006886
n2	0.5454	0.6055
χ^2	5.029E-4	2.378E-4
Meas. error	< 2.242pct.	< 1.542pct.

Electrochemical measurements in the two-electrode system: To fabricate a two-electrode symmetric solid-state device where both current collectors are made up of carbon cloth. The COF (50 mg; 80%), Super P carbon (15 mg; 15%) and 5% of PVDF binder (5mg) were added to mortar-pestle. It was ground thoroughly to make homogeneous after that, and an adequate amount of ethanol was added to it. A homogenous slurry was made by using mortar-pestle. This slurry was kept at 80 °C to evaporate the ethanol. Then the composite material was scratched and ground. The fine-powered composite material of 2.00 mg to 10.00 mg was measured through a balance (Sartorius Quintix35-1S semi microbalance) with a precision of 0.01 mg, kept in Eppendorf dispersed in 0.5 to 2 mL ethanol and sonicated for 2 hrs. It was drop-casted to an area of 1cm x 1cm of carbon cloth(1cm x 4cm) and dried. The traces left in the Eppendorf was redispersed in the ethanol and drop-casted. Moreover, we prepared three different batches of samples using the same protocol to fabricate the devices. The capacitance calculation has been done by using integral eq 3.

Note: We fabricated three devices from a different batch of samples with a total loading of 2 to 10mg for H_2SO_4 + KI gel, however for H_2SO_4 gel we made with 2 and 10mg only. The electrodes were dried at room temperature to remove the ethanol. Then, one side of the electrode was allowed to wet thoroughly by a gel electrolyte containing 1 M H_2SO_4 and 1 M H_2SO_4 + 0.2 M KI in polyvinyl alcohol (PVA). Two electrodes were made by the aforementioned procedure and were sandwich assembly was made by placing a Celgard separator in between. These solid-state supercapacitor devices were used for further electrochemical characterizations. Cyclic voltammetry (CV) measurements were performed at different scan rates from 2.5 to 500 mV/s by fixing a potential window in the range of 0 to 0.8 V Galvanostatic charge-discharge measurements were carried out at various current densities 0.5, 1, 2.5, and 5 mA/cm².

Preparation of the gel electrolyte: To prepare the gel electrolyte, 2 g of concentrated H_2SO_4 (98%) was added to 20 mL of millipore water, 2 g of PVA (polyvinyl alcohol) powders was added to it. The mixture was heated to 85 °C for about 30 minutes under continuous stirring until the solution became clear.

To prepare the KI + H_2SO_4 gel electrolyte, 2 g of concentrated H_2SO_4 (98%) was added to 20 mL of 0.2 molar KI (Potassium iodide) solution, 2 g of PVA (polyvinyl alcohol) powders were added to it. The mixture was heated to 85 °C for about 30 minutes under continuous stirring.

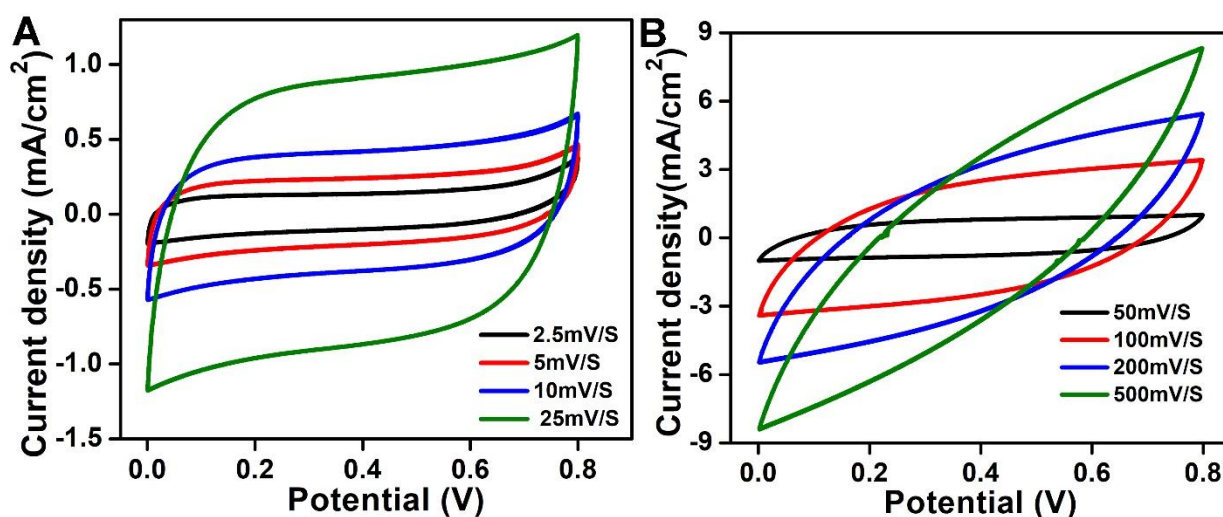


Figure A.2.20. Two-electrode CV measurements using IISERP-COF25 derived solid-state capacitor device (area 1 cm²) at different scan rates in PVA-H₂SO₄ gel electrolyte with a total loading 10 mg per device. (A) from 2.5 to 25 mV/s and (B) from 50 to 500 mV/s within the potential window of 0-0.8 V. Perfect rectangular-shaped CVs were obtained at lower current densities. Notably, the area under the CV curves does not decrease abruptly even in high scan rates (50 to 500 mV/s). Note: Here the electrolyte contains only 1 M H₂SO₄.

Capacitance estimation using the two-electrode solid-state assembly:

Discharge time obtained from the GCD curve was used for the estimation of the areal S_p . the capacitance of the COFs at different current densities (Nat. Commun. **2013**, 4, 2923., Sci Rep **2016**, 6, 25793., Adv. Energy Mater **2020**, 10, 2001673., J. Mater. Chem. A, **2013**, 1, 1086-1095.). Areal capacitance was calculated using the following equation

$$C_A = 2 \cdot I_s \cdot \frac{\int(V \cdot dt)}{a \cdot (\Delta V)^2} \dots \dots \dots \text{Eq A.2.3 (using Nonlinear GCD curve)}$$

where C_{sp} is the specific capacitance (mF/cm²) sample Where I_s = current density in mA/cm², $\int(V \cdot dt)$ = integral area of the discharging part of the GCD curve, 'a' is the geometrical area of the COF coated region on the electrode surface (cm²). ΔV = Potential window ($V = V_f - V_i$) and considering IR drop. To calculate the gravimetric capacitance (F/g), it is normalised by the total mass of the active electrode materials in both electrodes (mg).

Energy density and power density from the solid-state two-electrode system were calculated using the following equation

$$E_d = \frac{C_A}{2 \times 3600} V^2 \dots \dots \dots \text{Eq A.2.4.}$$

E_d is energy density (mWh/cm^2) CA is the areal capacitance calculated (mF/cm^2) by the charge-discharge method and V is the working potential window. Or

$$E_d = I_s \cdot \frac{\int(V \cdot dt)}{3600} \dots\dots\dots \text{Eq A.2.5}$$

where E_d is the specific capacitance (mWh/cm^2). Where I_s = current density in mA/cm^2 , $\int(V \cdot dt)$ = integral area of the discharging part of the GCD curve. To calculate the gravimetric energy density, it is normalised by the total mass of the active electrode materials in both electrodes (mg). Note: The energy density is found to be the same by calculation both equations.

$$P_d = \frac{E_d}{t} \dots\dots\dots \text{Eq A.2.6.}$$

P_d power density (mW/cm^2), E_d is the energy density (mWh/cm^2), 't' is the discharge time in hour calculated from the GCD curve.

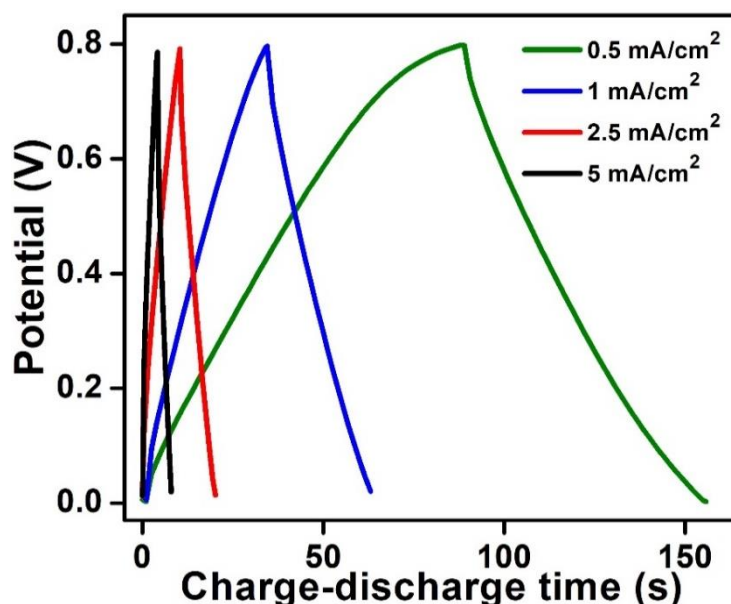


Figure A.2.21. Galvanostatic charge-discharge curves of the composite using solid-state two-electrode set-ups at variable current densities in a PVA- H_2SO_4 gel electrolyte. Note: Here the electrolyte contains only 1 M H_2SO_4 .

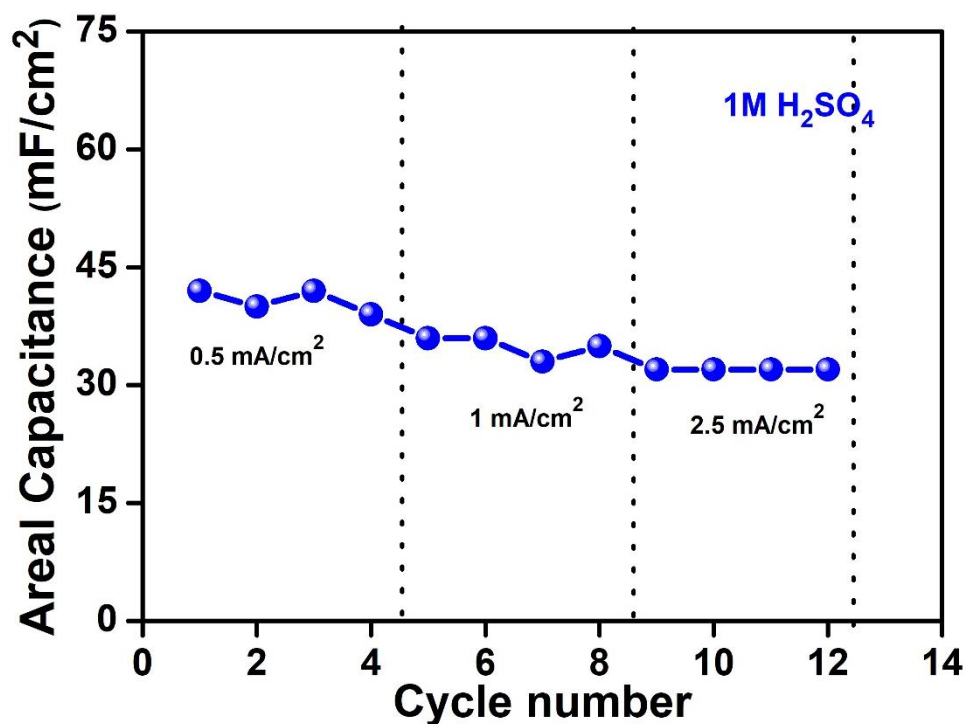


Figure A.2.22. The retention of the areal capacitance using PVA-H₂SO₄ with the increasing current density using two electrode solid device.

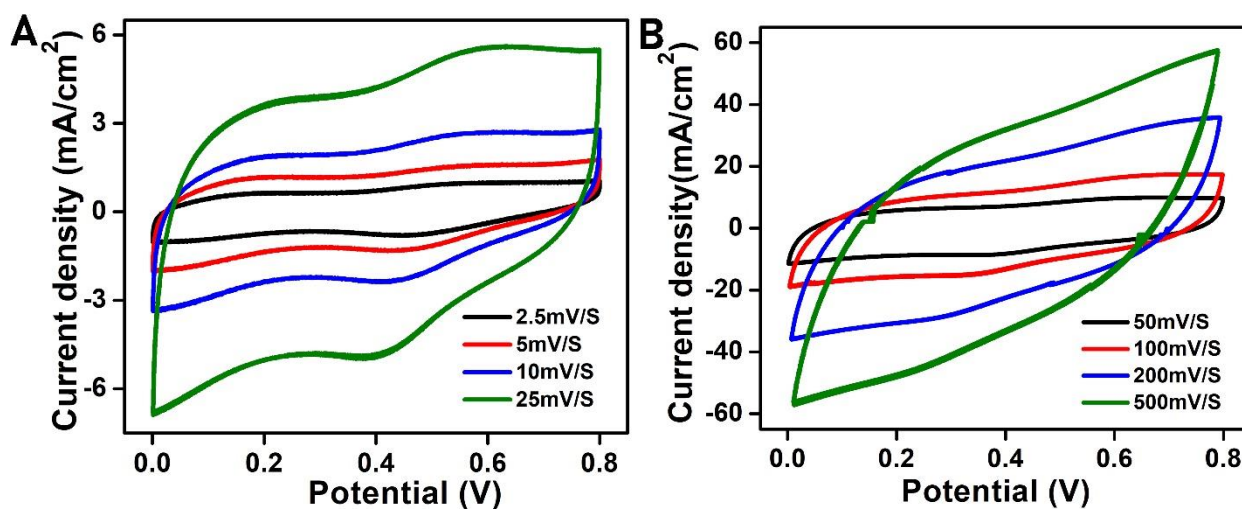


Figure A.2.23. Two-electrode CV measurements using composite derived solid-state capacitor device at different scan rates in PVA-H₂SO₄ + KI gel electrolyte with a total loading 10mg per device (A) from 2.5 to 25 mV/s and (B) from 50 to 500mV/s within the potential window of 0-0.8 V. Perfect rectangular-shaped CVs were obtained at lower current densities. Notably, the area under the CV curves does not decrease abruptly even in high scan rates (50 to 500 mV/s). Note: Here the electrolyte contains H₂SO₄ + KI.

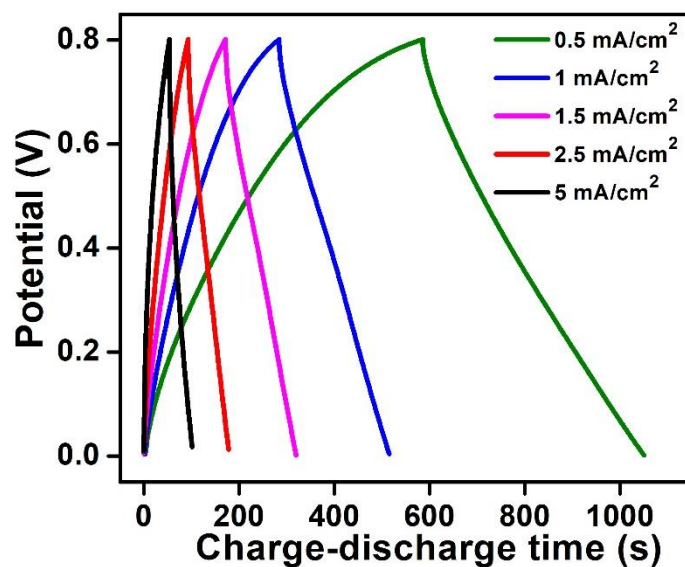


Figure A.2.24. Galvanostatic charge-discharge curves of the COF measured using the solid-state device at variable current densities with PVA-H₂SO₄ + KI gel electrolyte.

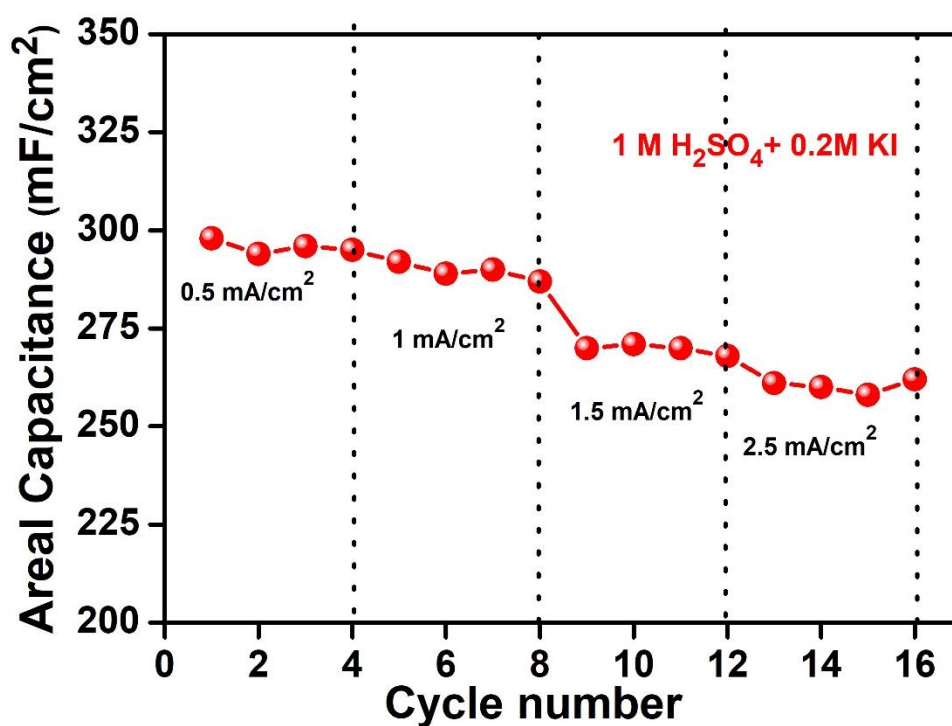


Figure A.2.25. The retention of the areal capacitance of solid-state two-electrode device made up of PVA-H₂SO₄ + KI gel electrolyte with increasing current density.

Table A.2.6. Energy and power densities of the composite based solid-state capacitors at $0.5\text{mA}/\text{cm}^2$ with 10mg of total loading per device.

Electrolyte system	Energy Density ($\mu\text{Wh}/\text{cm}^2$)	Power density ($\mu\text{W}/\text{cm}^2$)
1 M H_2SO_4	3.67 ± 0.34	209.30 ± 0.02
1 M $\text{H}_2\text{SO}_4 + 0.2\text{ M KI}$	23.68 ± 1.00	175.4 ± 3.27

Control studies:

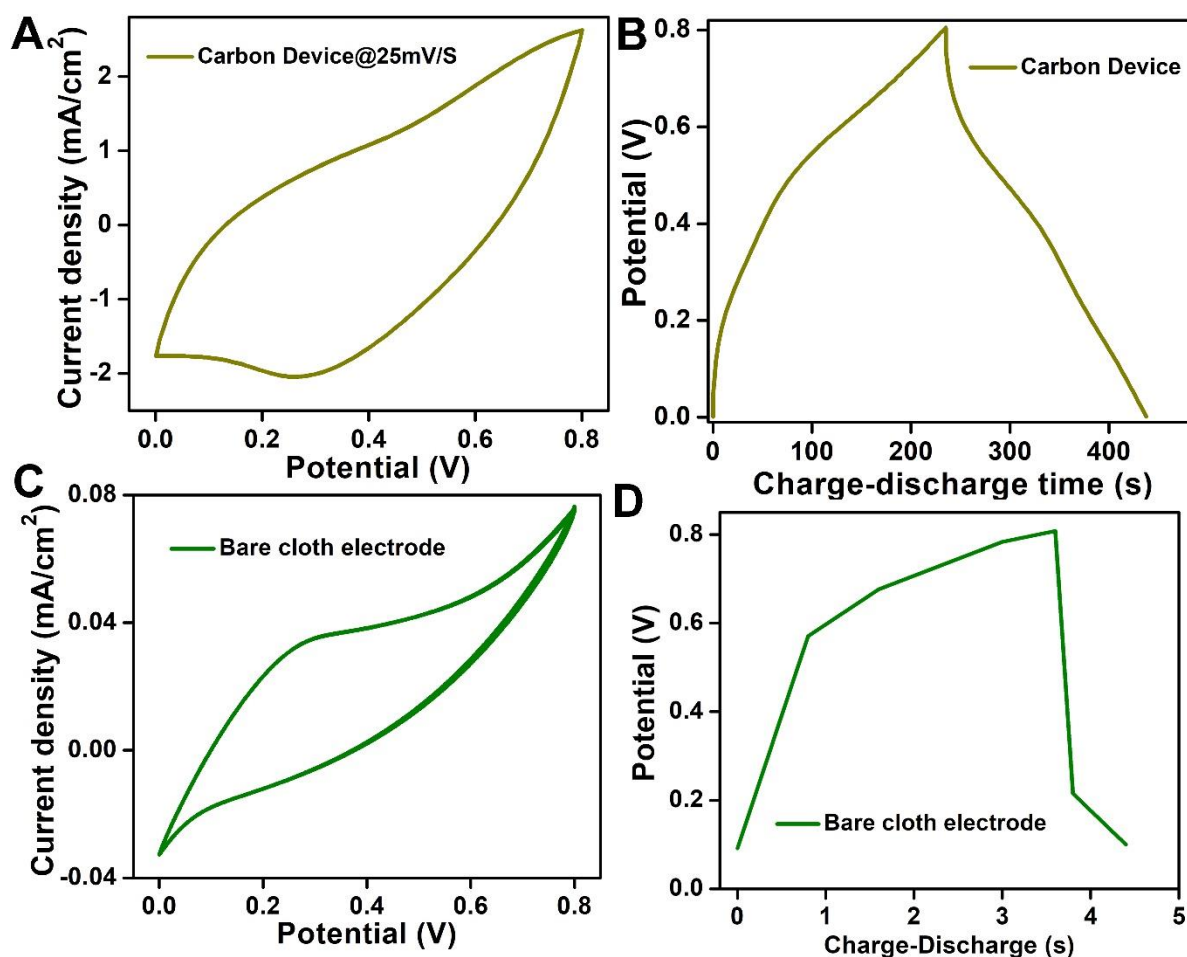


Figure A.2.26. (A) and (B) Symmetric solid-state capacitor fabricated with Super P carbon coated on the carbon cloth using the PVA- $\text{H}_2\text{SO}_4 + \text{KI}$ gel electrolyte with total loading 10mg per device in a two-electrode configuration. (A) CV measured @ $25\text{mV}/\text{s}$. (B) GCD curve obtained @ $0.5\text{ mA}/\text{cm}^2$ current density. (C) CV measurement @ $2.5\text{ mV}/\text{s}$ using only carbon cloth derived solid-state capacitors (without the active material, namely the IISERP-COF25) in $\text{H}_2\text{SO}_4 + \text{KI}$ electrolyte system. (D) GCD curve obtained @ $0.5\text{ mA}/\text{cm}^2$ current density using a carbon cloth-derived solid-state capacitor in the $\text{H}_2\text{SO}_4 + \text{KI}$ electrolyte system. *Note: The specific areal capacitance obtained from Super P carbon is $106.86\text{ mF}/\text{cm}^2$, which is low compared to $269.60 \pm 11.39\text{ mF}/\text{cm}^2$ obtained for the composite.*

Different flexible states of All solid-state supercapacitor

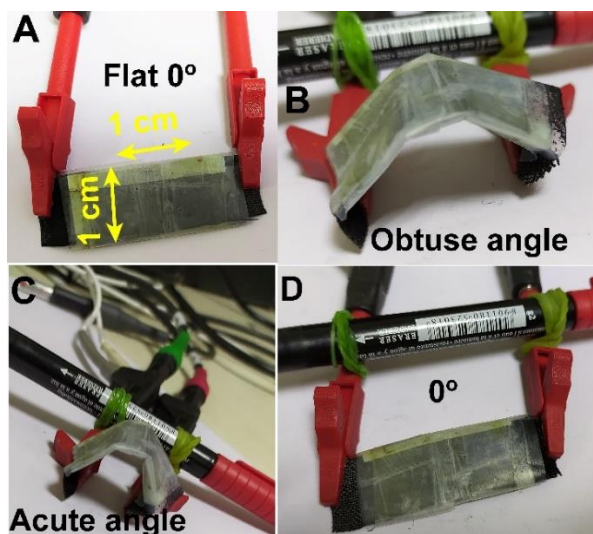


Figure A.2.27. Optical images of the flexible all-solid-state device under different flexible angles.

Insitu Spectroelectrochemistry:

Experimental Technique: First, the UV-Visible spectra of the $\text{KI-H}_2\text{SO}_4$ electrolyte solution was taken as the baseline. A dispersion of the COF in IPA was drop-casted on an ITO plate and this COF coated ITO plate was dipped into the electrolyte solution. The UV-Visible spectra of COF, taken in presence of electrolyte solution (where the baseline was already corrected with $\text{KI-H}_2\text{SO}_4$ electrolyte solution). Inside the UV cuvette, a typical three-electrode set up was built (similar to capacitor measurements) and connected to the ocean optics instrument to observe the change of the spectra insitu way. Then a chrono-amperometry measurement was carried out (at 0.8 V) up to two hours with the help of the CH instrument charge-discharge analyzer. At every 15 mins interval, the UV-visible spectra were recorded.



Figure A.2.28. The typical set-up of insitu spectroelectrochemistry.

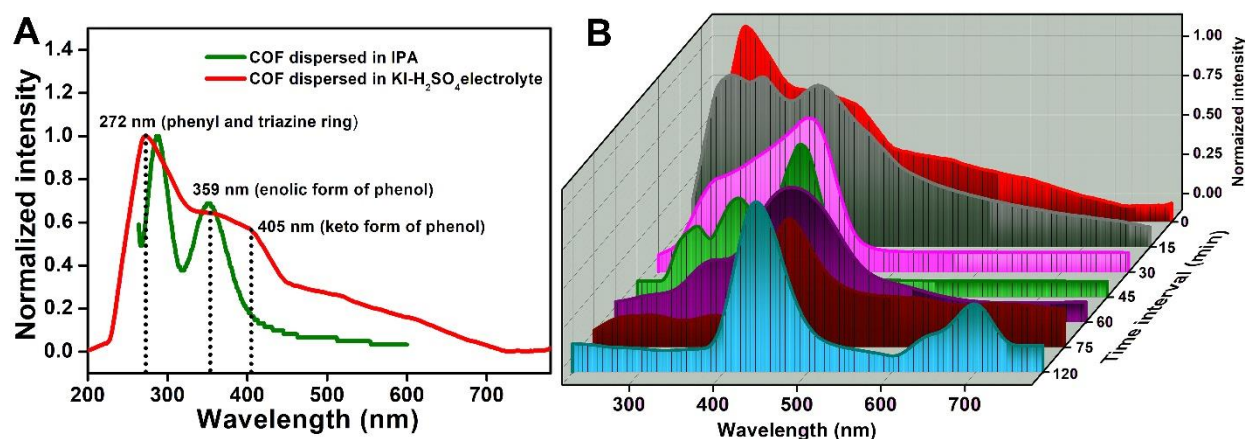


Figure A.2.29. (A) The comparison of insitu spectroelectrochemistry data of COF dispersed in IPA (Isopropyl alcohol) and dispersed in $\text{H}_2\text{SO}_4 + \text{KI}$ electrolyte. (B) The time-dependent insitu spectroelectrochemistry data of the COF recorded under an applied potential of 0.8 V.

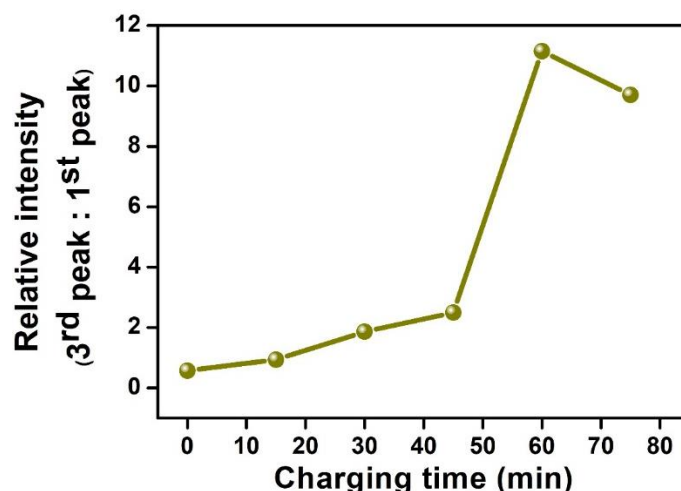


Figure A.2.30. The relative intensity of 3rd to 1st peak with time. The relative intensity of the 3rd peak increases at the expense of the decrease in the intensity of the 1st peak. This implies the strong interaction of I_3^- with the organic bone of the COF. This can be due to the interaction of the electron cloud of I_3^- with electron-deficient moieties of the COF. Also, there is a possibility to form an inclusion complex where I_3^- can be incorporated into the nano-channels of the COF.

Table A.2.7. Comparison of the characteristic peak shifts after the addition of $H_2SO_4 + KI$ at 0 V and 0.8 V.

Stretching band	COF dispersed in Isopropanol (Wavelength nm)	After the addition of $H_2SO_4 + KI$ at 0 V (Wavelength nm)	After addition of $H_2SO_4 + KI$ at 0.8 V (Wavelength nm) after 2hrs
Phenyl and triazine ring	288	272	295
Enolic form of phenol	352	359	366
Keto form of phenol	404	405	438
Charge transfer complex	-	-	698 nm

* Under applied potential the redshift of the whole spectra and gradual de-intensification brings out that the framework is interacting with the polyiodide species generated from the electrolyte under potential. The peak at 698 nm corresponds to charge transfer complex formation between some bridging $C-I^+-C$ and polyanionic species.

In situ Raman spectroscopy:

Figure S43 shows the typical set-up of the In situ Raman spectroscopy that we used for these measurements. The COF was pressed into a pellet (thickness $\sim 75 \mu m$) onto the surface of a conductive ITO electrode. A custom-made PDMS well was used to load the electrolyte. All the experiments were conducted in a three-electrode geometry with Ag/AgCl as the reference electrode and Pt wire as the counter electrode. All Raman spectra were collected in a confocal geometry with a 532 nm excitation laser (2 mW) focusing on the surface of the COF-pellet.

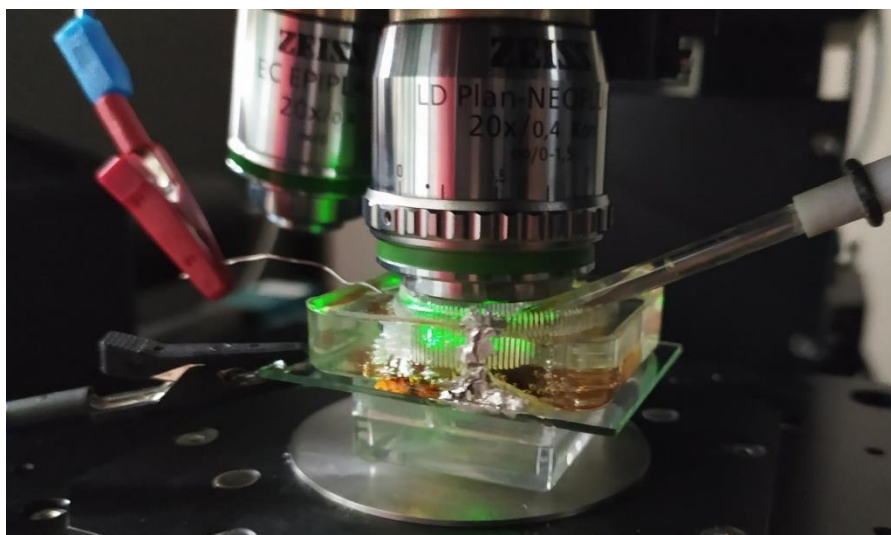


Figure A.2.31. The typical set-up of the In Situ Raman Spectroscopy measurements.

Our COF is fluorescent, so we couldn't record the proper Raman spectra of the as-made COF. But the quenching of fluorescence has been observed upon the addition of $\text{H}_2\text{SO}_4 + \text{KI}$ to the COF system. Small but discernible shifts in peak positions were observed under potential and without potential.

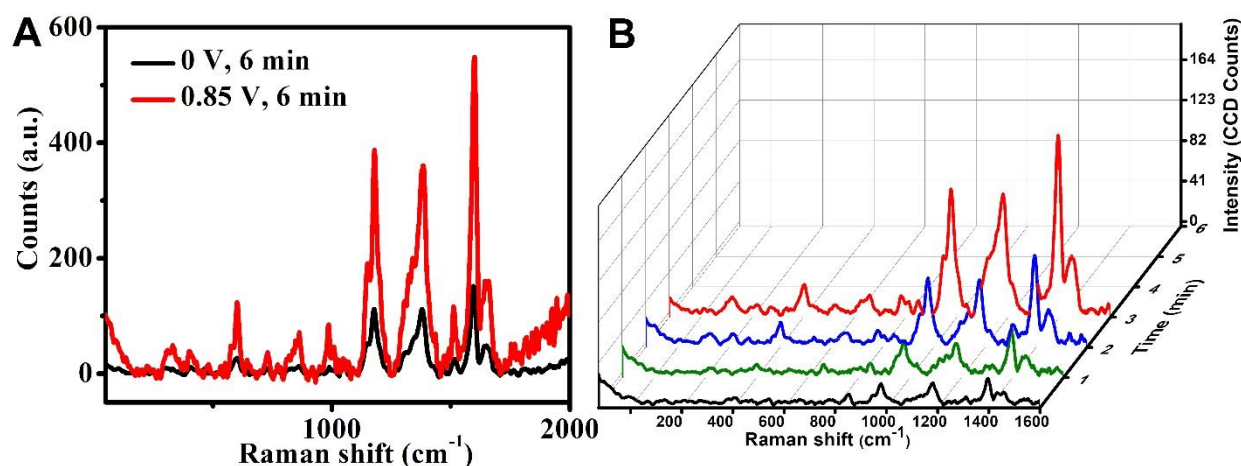


Figure A.2.32. (A) The comparison of In Situ Raman spectra after the addition of $\text{H}_2\text{SO}_4 + \text{KI}$ at 0 V and 0.8 V after 6 mins. (B) The In Situ Raman has taken at different time intervals at 0.8V.

Table A.2.8. Comparison of the characteristic peak shifts after the addition of $\text{H}_2\text{SO}_4 + \text{KI}$ at 0 V and at 0.8 V.

Stretching band	After the addition of $\text{H}_2\text{SO}_4 + \text{KI}$ at 0 V (Frequency in cm^{-1})	After the addition of $\text{H}_2\text{SO}_4 + \text{KI}$ at 0.8 V (Frequency in cm^{-1})
C=C	1595	1599
C=O	1610	1615
C=N	1665	1658
C-I	-	320 (overtone band 600)

* Peaks at 1500 cm^{-1} observed due to symmetry breaking of C=C bond upon Iodination to COF.

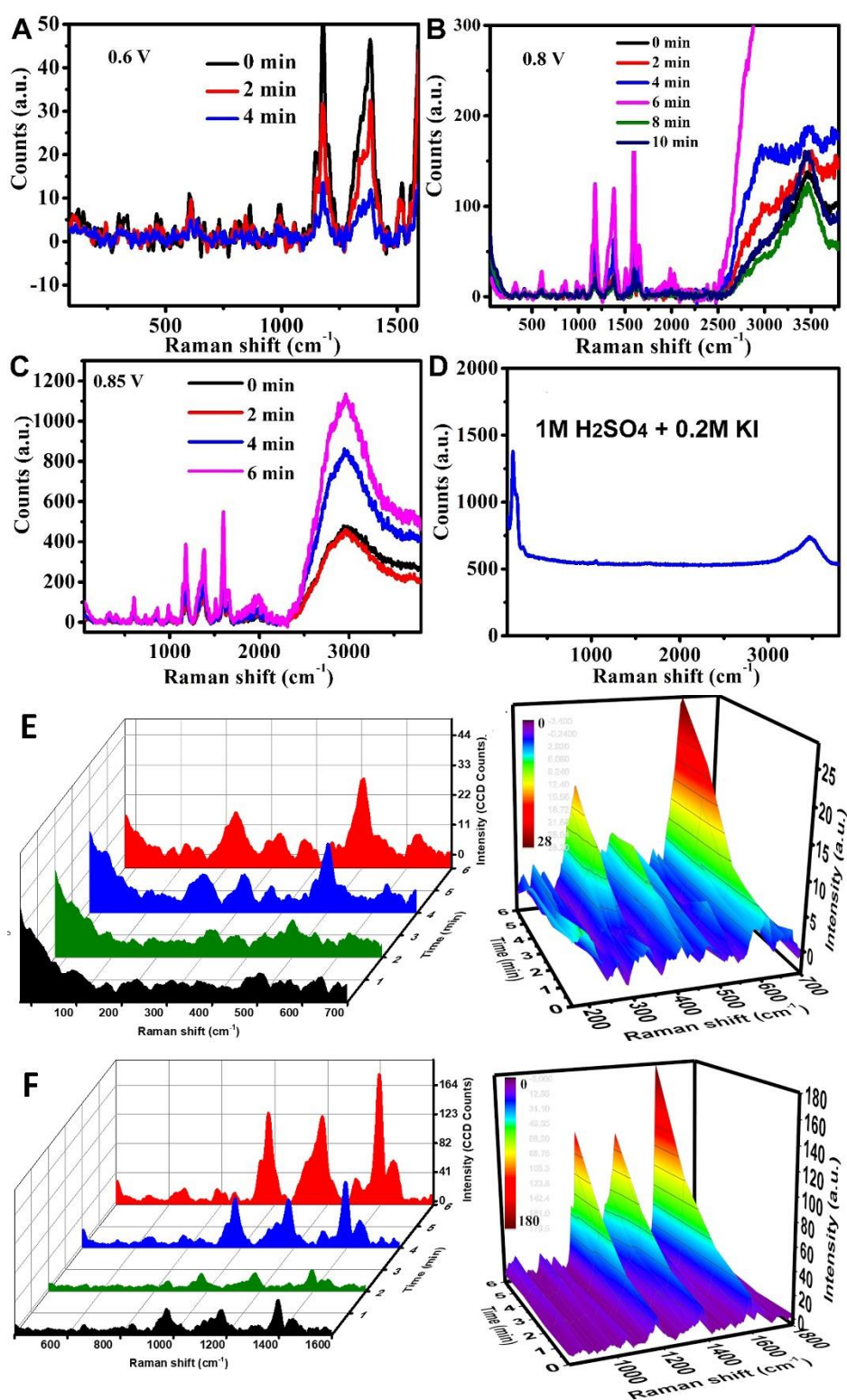


Figure A.2.33. (A), (B), and (C): The comparison of in situ Raman spectra after the addition of H_2SO_4 + KI at different intervals of time at 0.6 V, 0.8 V, and 0.85 V respectively. (D) The control in situ Raman spectra taken only with H_2SO_4 + KI at 0.8 V. (E) Change in Raman peak intensity as a function of time (100-700 cm^{-1} region). (F) Change in Raman peak intensity as a function of time (600-1600 cm^{-1} region).

X-ray photoelectron spectroscopy (XPS)

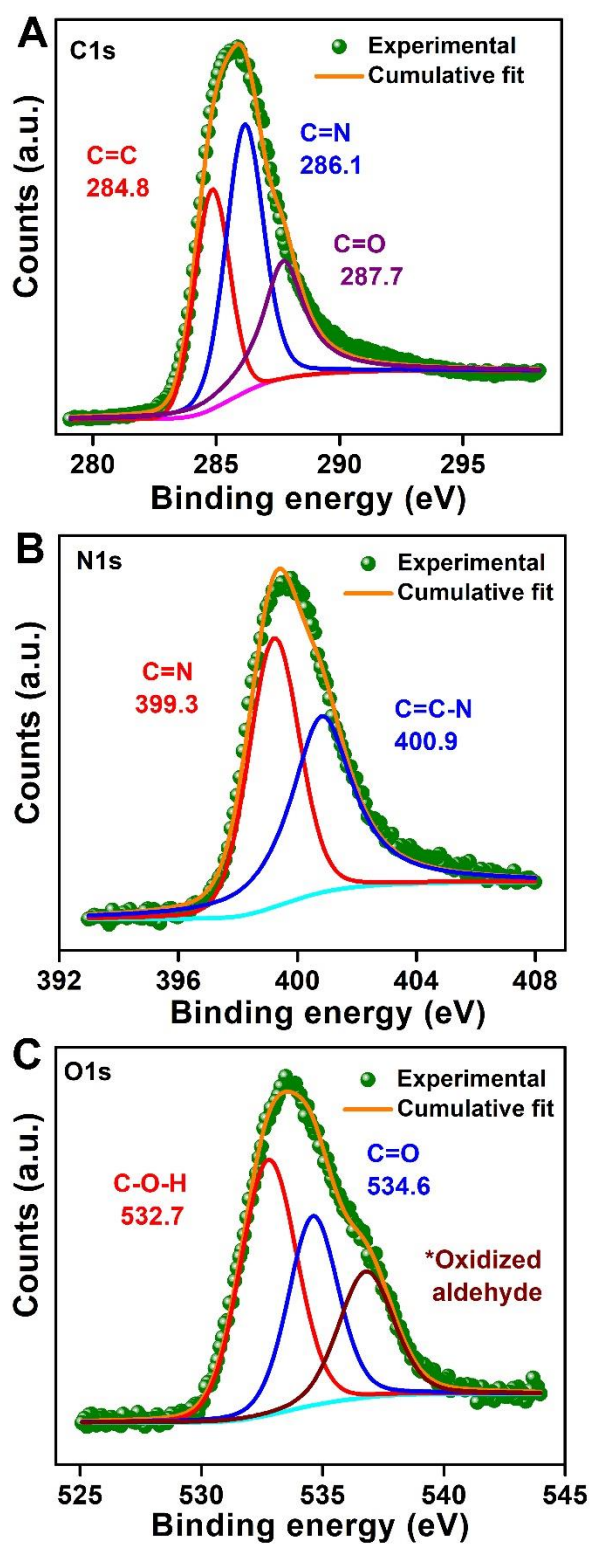


Figure A.2.34. X-ray photoelectron spectroscopy (XPS) of the as-synthesized COF.

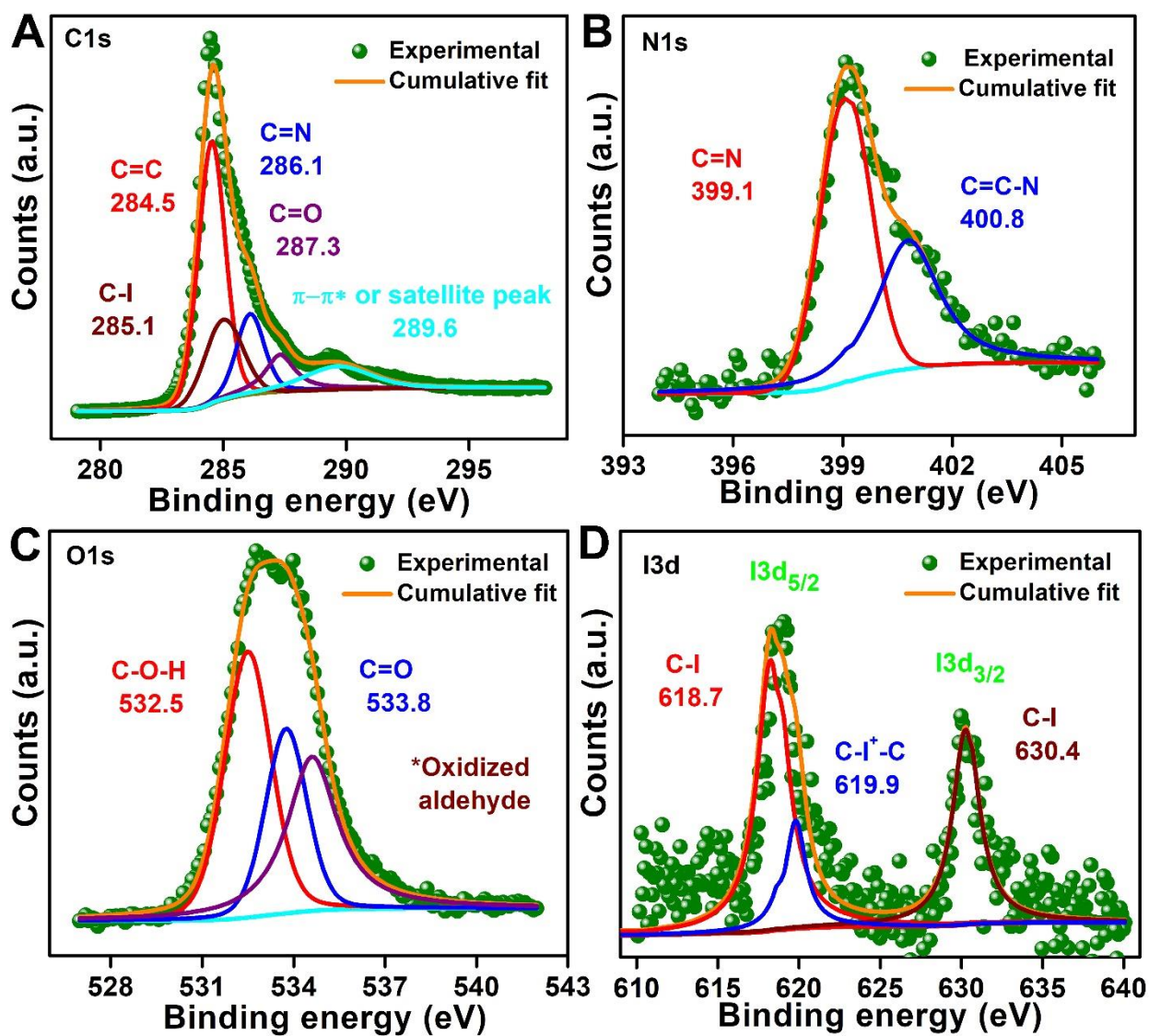


Figure A.2.35. XPS spectra of a charged solid-state device fabricated with COF slurry and KI + H₂SO₄ gel electrolyte.

Two-electrode solid device:

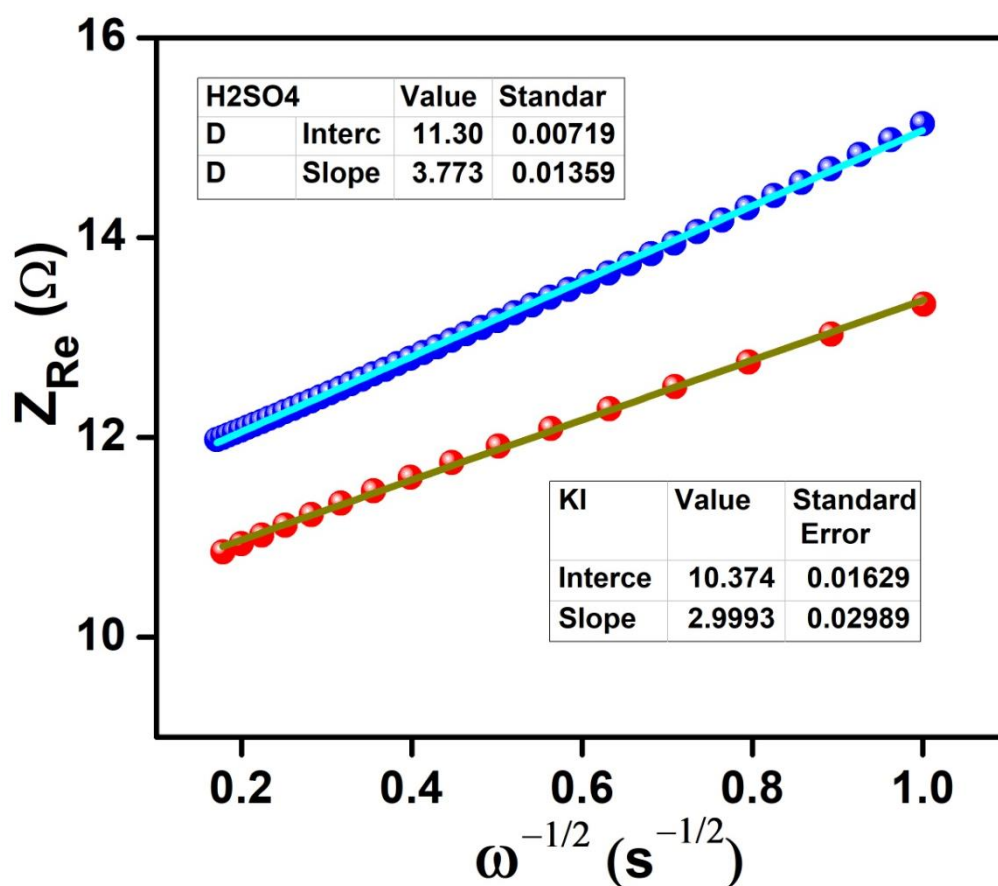


Figure A.2.36. A plot of the Z_{Re} vs. Inverse square root of frequency (ω) of solid device 1 M H_2SO_4 and 1 M H_2SO_4 + 0.2M KI PVA gel electrolyte.

Table A.2.9. Comparison of circuit elements of composite-based solid electrode device with H_2SO_4 gel and H_2SO_4 + KI gel.

Circuit elements	Solid device (H_2SO_4 gel)	Solid Device (H_2SO_4 +KI gel)
Rs (ohm)	11	9.919
Rct (ohm)	0.7	0.15
Q1	0.001778	0.04499
n1	0.7861	0.84
Wo	0.1608	0.0001298
Q2	0.06241	0.01851
n2	0.7274	0.7
χ^2	3.518E-5	0.0005906
Meas. error	< 0.5932pct.	< 2.43pct.

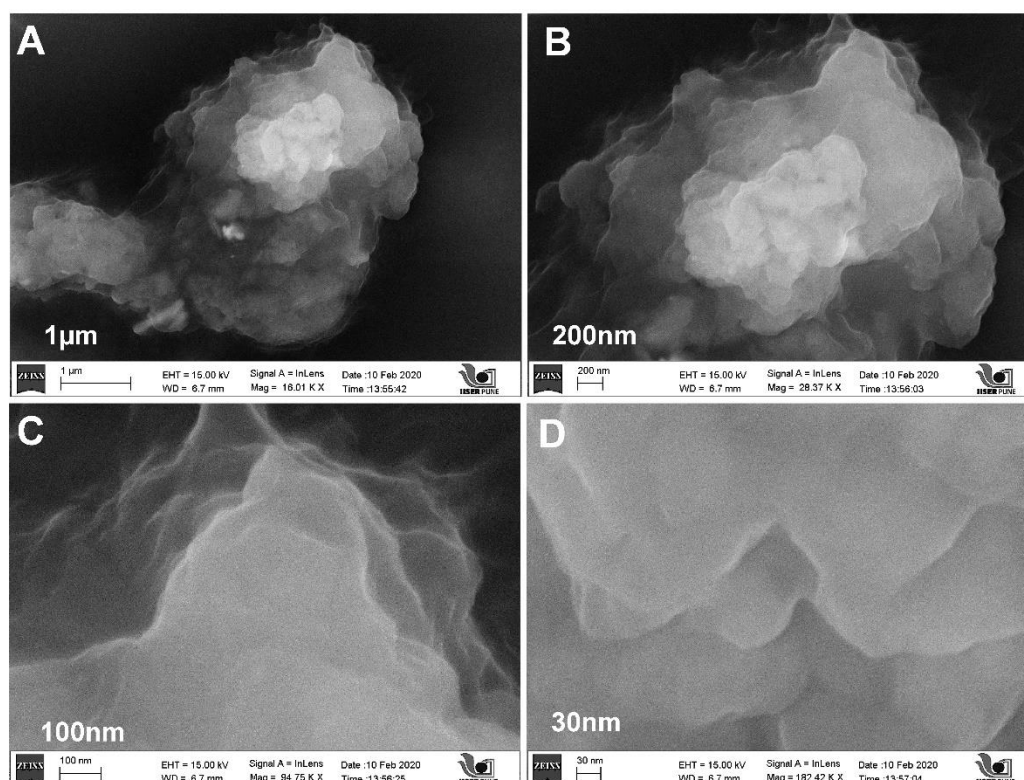


Figure A.2.37. FESEM images of IISERP-COF25 coated on the working electrode of three-electrodes systems at different resolutions. It washed thoroughly with water and methanol and dried into a vacuum oven at 80 °C, and then it was drop-casted on a silica wafer. It shows fluffy cotton-like morphology.

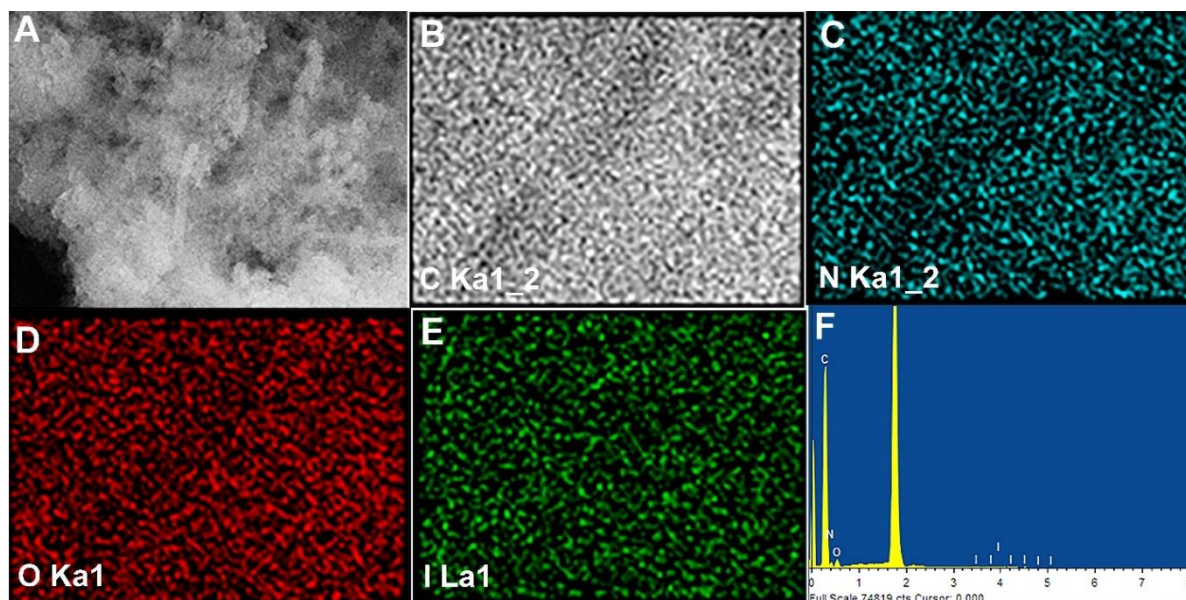


Figure A.2.38. The elemental mapping reveals the homogeneous distribution of iodine on the sample extracted from the working electrode of the three-electrode system.

Elements	Weight%	Atomic%
C K	73.19	78.03
N K	14.08	12.87
O K	11.17	8.94
I L	1.56	0.16
Totals	100.00	

Figure A.2.39. The EDAX analysis shows the percentage of Iodine present in the material scratched from the working electrode of the three-electrode system.

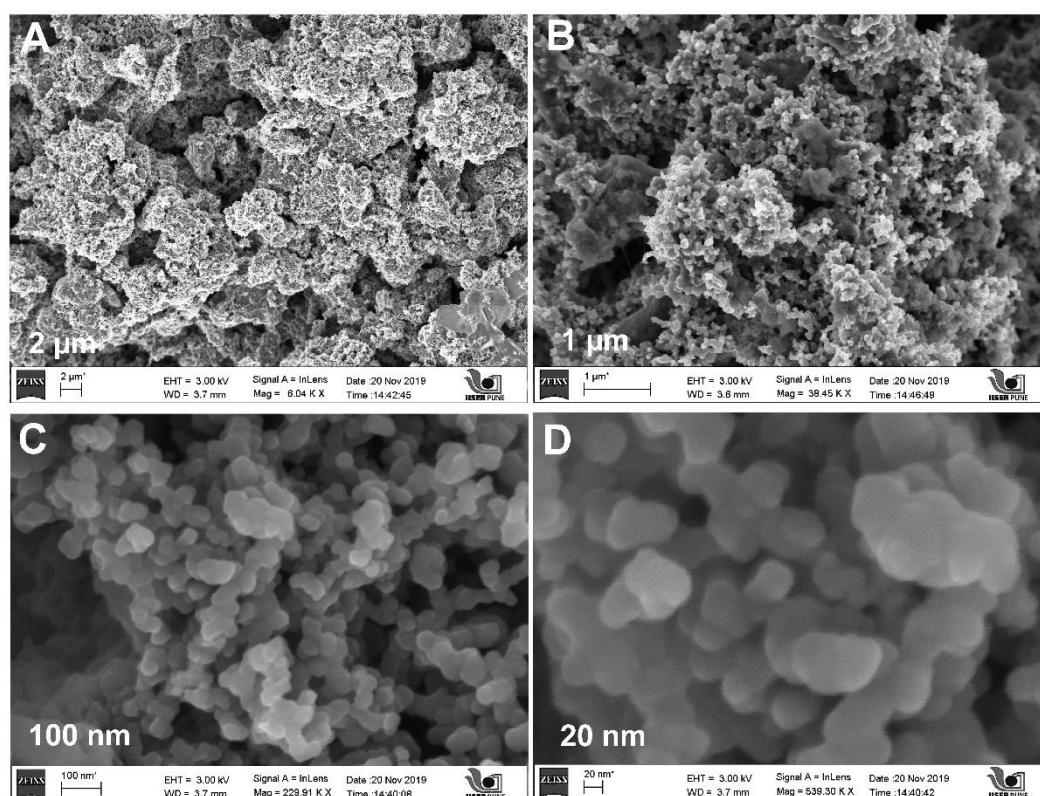


Figure A.2.40. FESEM images of IISERP-COF25 coated on the electrode of the two-electrode device at different resolutions. A small portion of the electrode cut from the charged device was directly subjected to imaging without washing.

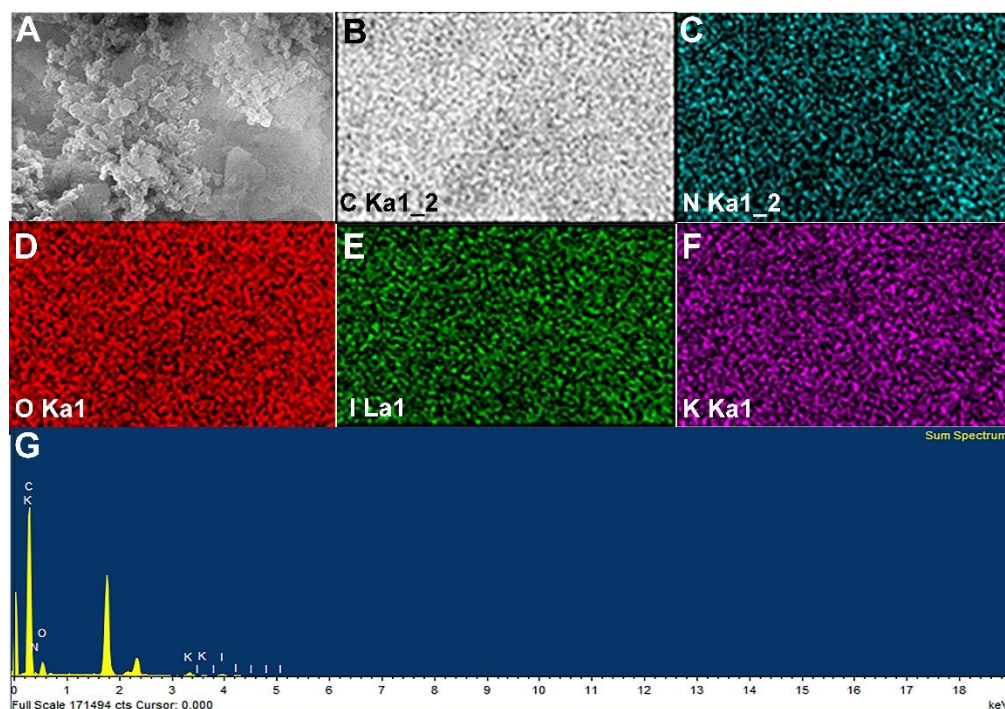


Figure A.2.41. The elemental mapping reveals the homogeneous distribution of Carbon, Nitrogen, Oxygen, Iodine, and Potassium on the small portion of the electrode of a two-electrode device without washing.

Elements	Weight%	Atomic%
C K	72.10	78.82
N K	8.90	8.34
O K	14.76	12.11
K K	1.27	0.43
I L	2.98	0.31
Totals	100	

Figure A.2.42. The EDAX analysis shows the percentage distribution of Carbon, Nitrogen, Oxygen, Iodine, and Potassium on the small portion of the electrode taken from charged two-electrode devices without washing. **Note:** The standard deviation has been calculated for Iodine from samples subjected to charging cycle. Samples from three different two-electrode devices have been used. The mean and standard deviation for weight % is found to be 2.13 ± 0.56 and 0.98 , and for atomic % is 0.23 ± 0.06 and 0.11 .

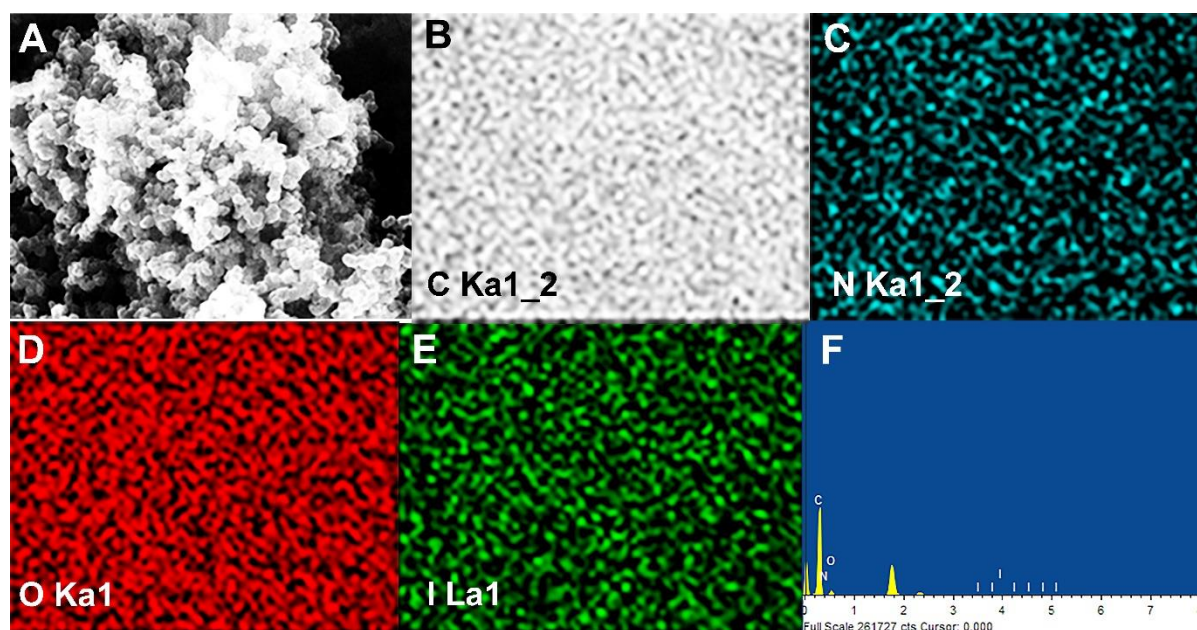


Figure A.2.43. The elemental mapping reveals the homogeneous distribution of Carbon, Nitrogen, Oxygen, Iodine, and Potassium of material extracted from and washed from charged two-electrode devices.

Elements	Weight%	Atomic%
C K	72.54	77.67
N K	8.36	7.67
O K	18.11	14.56
I L	0.99	0.10
Totals	100.00	

Figure A.2.44. The EDAX analysis shows the percentage distribution of Carbon, Nitrogen, Oxygen, and Iodine of washed material scratch from charged two-electrode devices. **Note:** The mean and standard deviation have been calculated for the Iodine% from three different two-electrode devices. The standard deviation for weight % is found to be 1.42 ± 0.22 and 0.38 , and for atomic % is 0.14 ± 0.02 and 0.04 . Note: The similar type of fractional value reported in Wang et al *J. Am. Chem. Soc.* **2018**, 140, 39, 12345–12348. Shirsath et al *J Nanopart Res* **2013**, 15, 1976.

Variation of Mass loading in two-electrode devices:

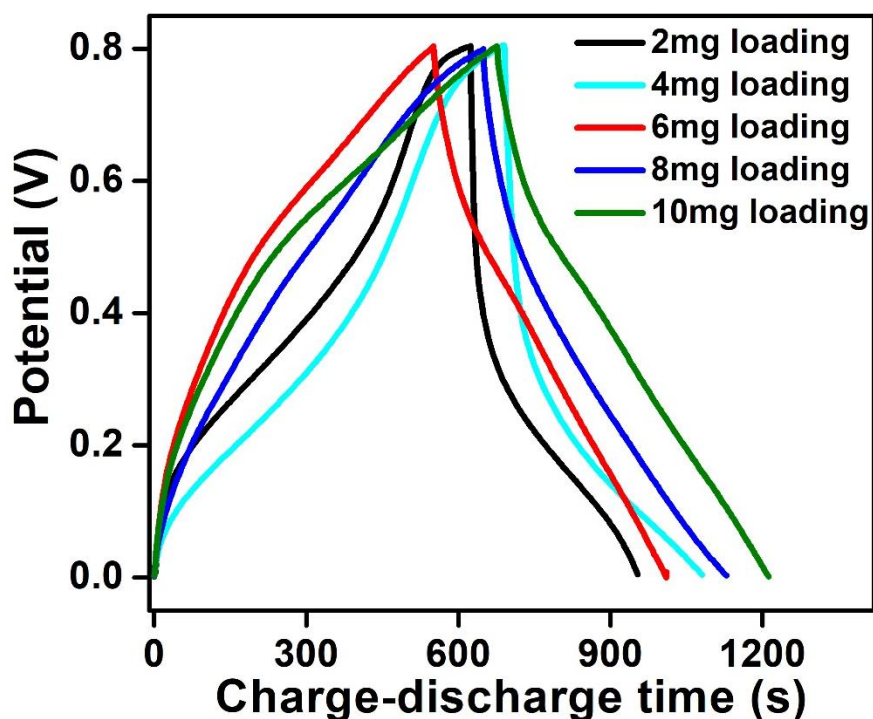


Figure A.2.45. Galvanostatic charge-discharge curves of the three different solid-state devices made up of composite (COF+carbon) with PVA-H₂SO₄ + KI gel electrolyte and different mass loading per device at 0.5mA/cm² current density.

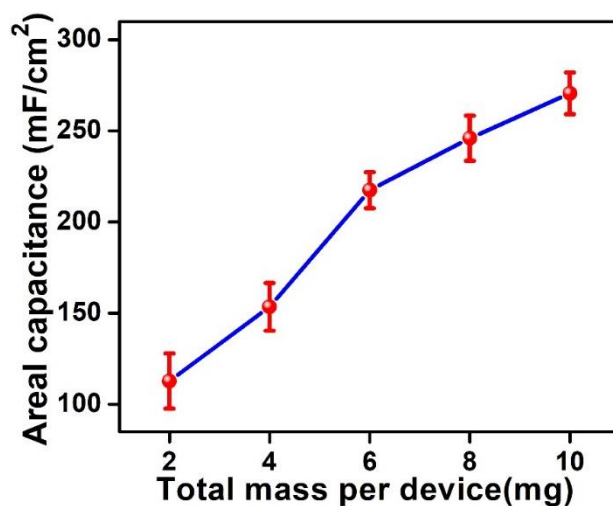


Figure A.2.46. Areal capacitance vs total mass loading per device obtained from three different devices of each mass loading fabricated with composite (COF + carbon) and PVA-H₂SO₄ + KI gel electrolyte by galvanostatic charge-discharge at 0.5mA/cm² current density.

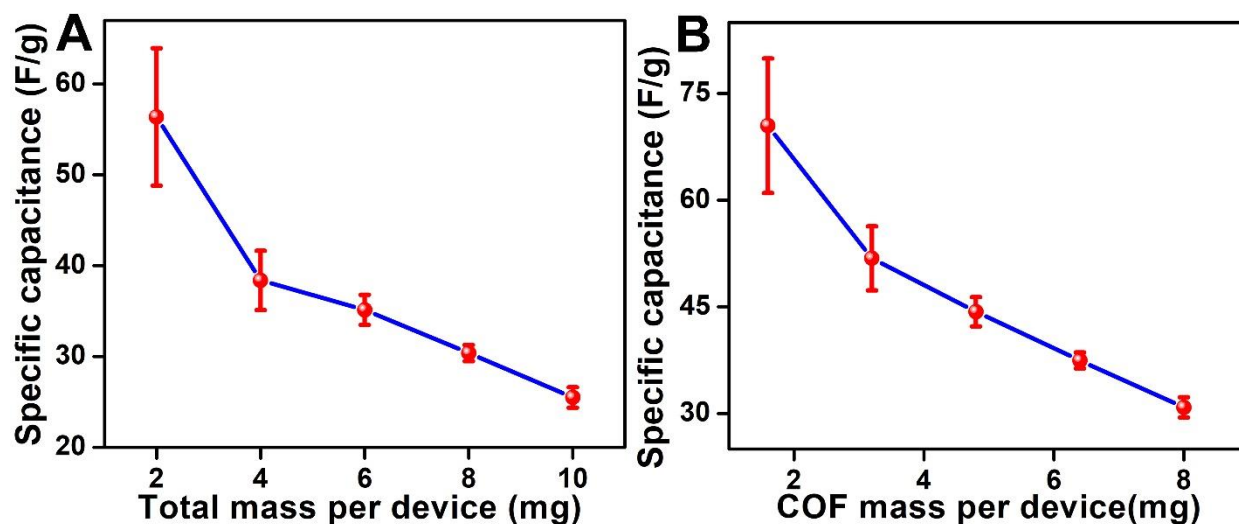


Figure A.2.47. (A) Specific capacitance vs total mass loading per device obtained from three different devices of each mass loading fabricated with composite (COF + Super P carbon + binder) and PVA- H_2SO_4 + KI gel electrolyte by galvanostatic charge-discharge at $0.5\text{mA}/\text{cm}^2$ current density and normalised by the total mass of the device. (B) Specific capacitance vs COF mass loading per device obtained from three different devices of each mass loading fabricated with composite (COF) and PVA- H_2SO_4 + KI gel electrolyte by galvanostatic charge-discharge at $0.5\text{mA}/\text{cm}^2$ current density and normalised by COF mass of the device.

Table A.2.10. Performance evaluation of composite-based symmetrical solid-state capacitors with mass loading per device.

Total loading per device	2 mg loading		10 mg loading	
Amount used for calculation	COF+Carbon (100%) loading	COF (80%) loading	COF+Carbon (100%) loading	COF (80%) loading
Areal capacitance (mF/cm^2)	112.75 ± 15.15	-	269.60 ± 11.39	-
gravimetric capacitance (F/g)	56.37 ± 7.57	70.47 ± 9.47	27.0 ± 1.14	33.70 ± 1.42
Gravimetric energy density (Wh/Kg)	4.95 ± 0.67	6.29 ± 0.74	2.37 ± 0.10	2.89 ± 0.19
Gravimetric power density (W/Kg)	51.59 ± 4.01	65.64 ± 3.87	18.34 ± 0.08	21.94 ± 0.95

All measurements presented in this table were done at $0.5\text{ mA}/\text{cm}^2$ and normalized to the total mass loading of material per device. Highest reported gravimetric capacitance of a COF-derived asymmetric solid-state capacitor from literature: 64 F/g @ 1 A/g (S8).

Stability of the composite-electrode (COF + Carbon + NAFION binder) subjected to multiple cycles:

For this purpose, about 80 mg of the COF was mixed with 15 mg of Super P carbon and 100 microL of Nafion binder. The contents were ground in a mortar-pestle with 2 mL of ethanol. The resulting slurry was coated onto a 4 cm x 2 cm Pt mesh. Thus prepared dried mesh was used as the working electrode, a Pt flag was used as the counter and the Ag/AgCl was used as the reference. Cyclic voltammograms were recorded using this three-electrode configuration. The cyclic voltammetry experiment has been performed in 1 M H_2SO_4 + 0.2 M KI solution for 700 and 10000 cycles. After completion of the experiment, the active electrode material was scratched from the electrode and dried. The scratched composite was characterized by PXRD, FESEM, HRTEM, IR, and XPS to check the stability of the material.

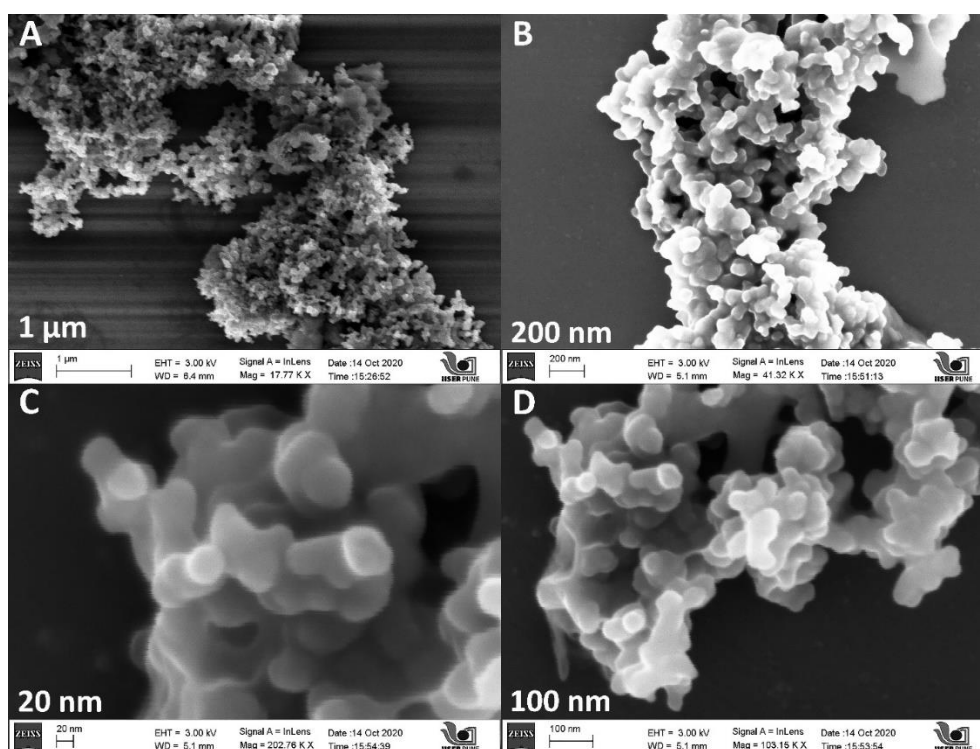


Figure A.2.48. FESEM images of composite coated on the Pt mesh working electrode of three-electrodes systems obtained after 10000 cycles of CV at different resolutions. It washed thoroughly with water and methanol and dried into a vacuum oven at 80 °C, and then it was drop-casted on a silica wafer. It shows fluffy cotton-like morphology.

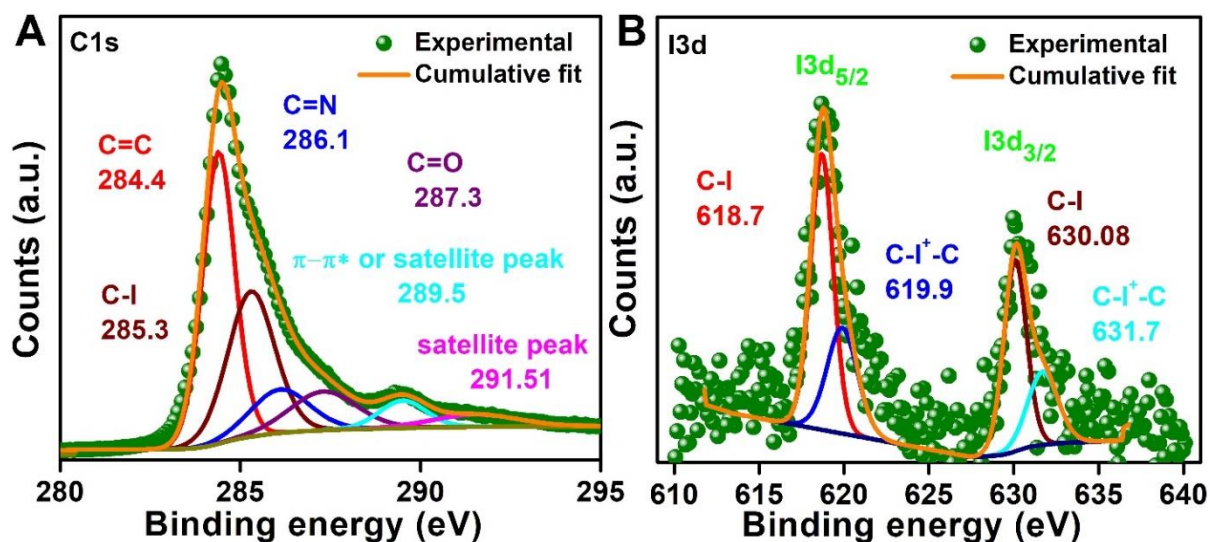
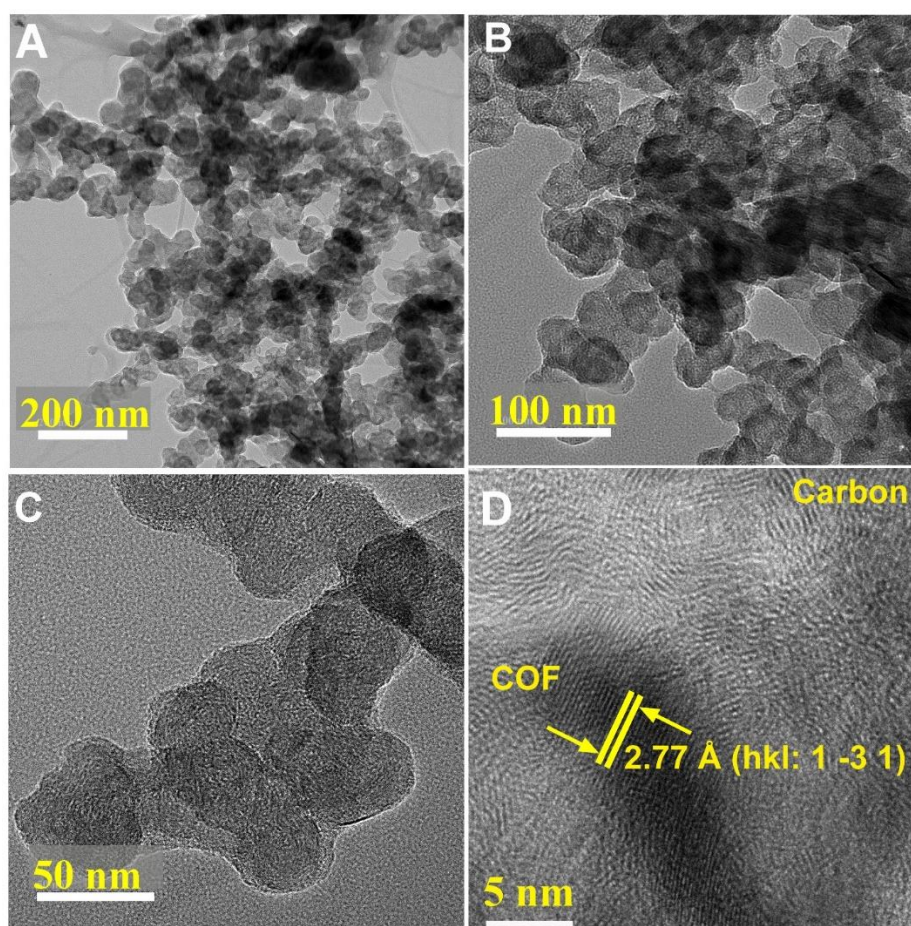


Figure A.2.49. XPS spectra of Composite material scratched from Pt after 10000 cycles of cyclic voltammogram 1 M H₂SO₄ + 0.2 M KI solution.



Figures A.2.50. HRTEM images of the composite subjected to 10000 CV cycles (A) Several amorphous carbon particles can be seen along with some COF flakes. (B) A higher resolution image showing the amorphous carbon (SAED or lattice fringes could not be observed). (C) Several COF flakes with some carbon (darker) can be seen. (D) The lattice fringes from COF flakes buried among carbon can be seen. The above SAED pattern is from one such crystalline COF flake.

Post electrochemical sample analysis after 700 cycles:

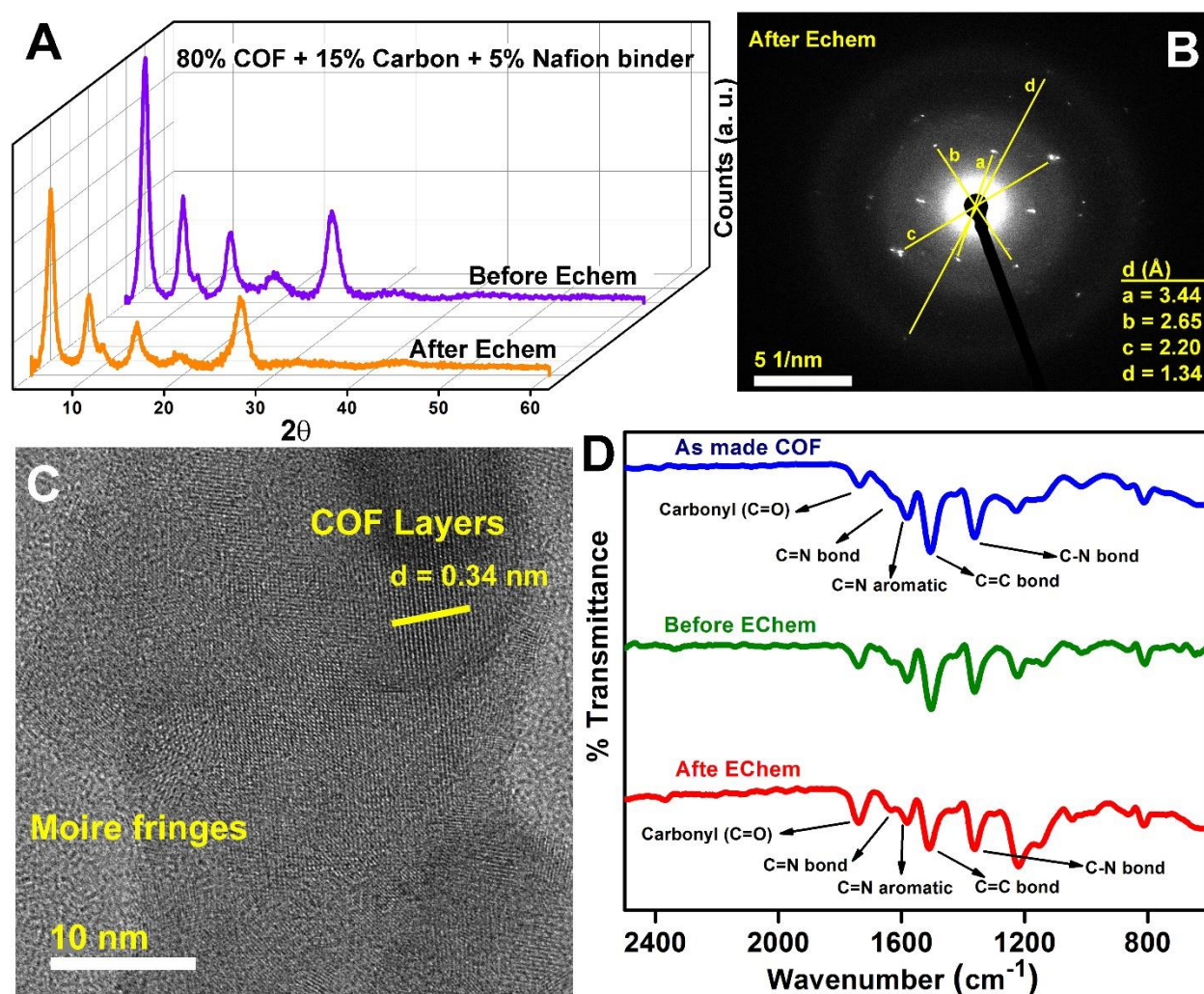


Figure A.2.51. (A) A comparative PXR D pattern of the composite before and after subjecting to 700 CV cycles using H_2SO_4 + KI as the electrolyte. (B) and (C) SAED pattern and high-resolution TEM images of the composite subjected to 700 CV cycles showing the crystallinity of the flakes. The presence of carbon flakes on the COF surface could also be observed. (D) Comparative IR spectra of the pre- and post-CV composite showing functional group preservation.

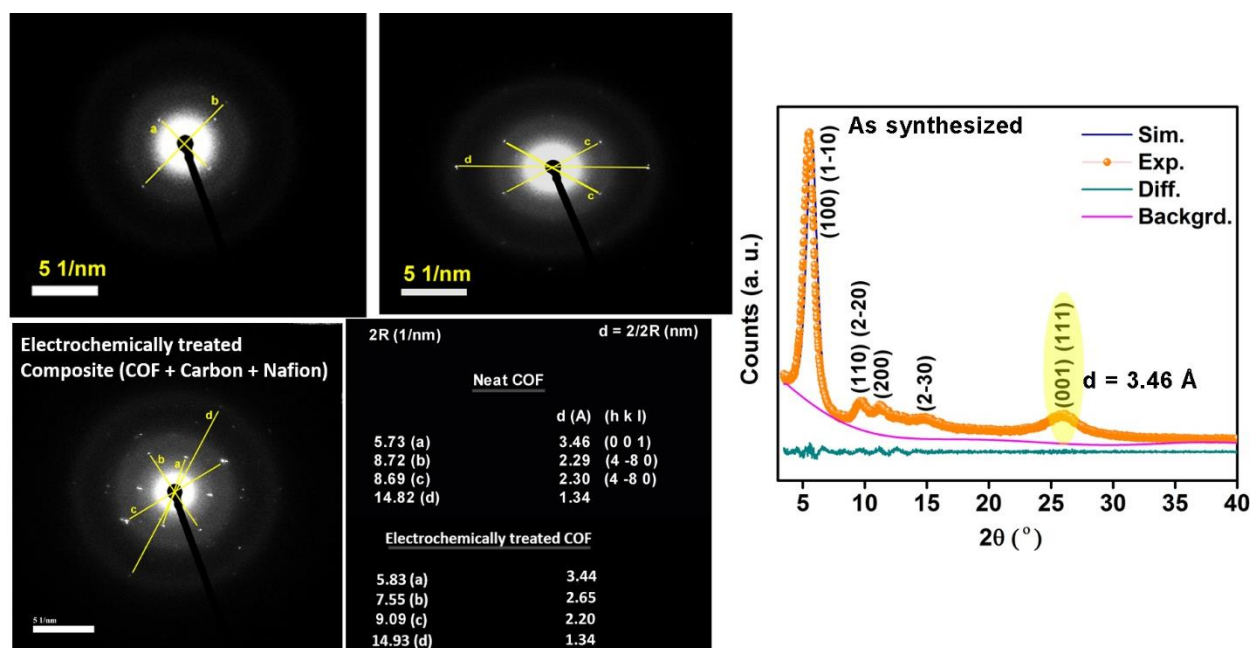


Figure A.2.52. The SAED pattern of the composite subjected to 700 CV cycles and the neat COF are shown and there are reflections from both which have d-spacing which can be attributed to the interlayer spacing of the COF layers (model: 3.53 Å). Also, other comparable reflections are seen from both as-synthesized COF and the electrochemically treated composite. However, there are some changes.

Remark on device performance comparisons:

The three-electrode system works with a near-perfect reference electrode, which does not allow current to pass and provides a stable potential with respect to which the potential of the working electrode is measured. Since the reference electrode passes negligible current, the iR drop between the reference and working electrode is often minimal. Thus with the three-electrode system, the reference potential is much more stable, and there is compensation for iR drop across the solution. This translates into superior control over the working electrode potential. This half-cell configuration thus helps to estimate the maximum charge storage ability of the working electrode. But not necessarily the practical capacity.

Typically, a large current passes through an electrode in a parallel plate capacitor (two-electrode symmetric systems where the working and reference electrodes are identical). The potential changes due to the iR drop, where the R is the resistance of the electrolyte, and i the current passing for the circuit. Typically, in a two-electrode configuration (full-cell), the iR drop can be minimized by lowering the distance between the two electrodes or using ultramicroelectrodes, in which the current measured is very small. In our solid-state capacitor, we pressed the two electrode systems to minimize the gaps between electrodes. Moreover, devices in practical life applications are made of the two electrode systems. So it is better to report the two-electrode performance of the device for comparisons.

Table A.2.11. Performance comparisons three set up and two electrode solid state device

	Three electrode (H ₂ SO ₄ +KI)	Two electrode (H ₂ SO ₄ +KI)
Charge stored(C/g)	1469.01±127.87	45.10 ±6.06 (2mg loading)
Charge stored (C/cm ²)	-	215.68 ±9.11 (10mg loading)

Computational details:

Optimization of the lowest energy configurations for the Polyiodide and H_3O^+ loaded phases using Simulated Annealing modus operandi: The Monte-Carlo methods were used to obtain the most probable locations of the H_3O^+ , I_3^- and $(\text{I}_3^- + \text{H}_3\text{O}^+)$ species within the low-energy configuration of the protonated COF. These were carried out using the Simulated Annealing techniques available within the Materials Studio V.6.0. For the H_3O^+ the saturation loading of 5 H_3O^+ per unit-cell of the COF was used. For the I_3^- , I_2 and I^- , two units per unit cell was used. These numbers were employed to mimic the concentrations used in the experimental measurements. For the Simulated Annealing, default parameters were utilized. Automatic temperature control and 100000 cycles/cell were employed to optimize the structure. Universal force field (UFF) in conjugation with a Q_{Eq} charge equilibration method was employed for the geometry optimization, however, we noticed that applying the equilibration (Q_{Eq}) did not make much of a difference to the final configurations. A cubic-spline truncation method with a charge group cut-off of 18.5 Å was employed. Accuracy was set to 1 e-005 kcal/mol. No constraints were placed during the optimizations. Excellent convergence was achieved for all cases.

The optimized geometry under an applied external electric field were calculated using the CASTEP routine (First principles methods using CASTEP, Zscheischrift fuer Kristallographie, 220, 5, 567 (2005)). For this the GGA functional (Perdew Wang, 1991) was employed with a basis cut off of 260 eV. Pulay density mixing scheme and a Gaussian smearing scheme with a smearing width of 0.1 eV were used. The energy tolerance was set at 1×10^{-5} eV/atom. The spin were allowed fully relax for all steps. Ultrasoft pseudopotentials were employed. An external electric potential of 0.05 eV/Å/e was applied in all cases (Ghoufi et al, *ACS Cent. Sci.* 2017, 3, 5, 394–398; and Li et al, *RSC Adv.*, 2017, 7, 56676). Notable changes in unit cell dimensions were observed in case of the structures incorporating guest iodides or iodine. In case of I_3^- the pores in the optimized structure shrink increasing the COF interactions with and the polyiodide and H_3O^+ (Ghoufi et al., *ACS Cent. Sci.* 2017, 3, 5, 394–398). In all cases, the COF-guest interactions are favorable reflected also in the lowest total energy, and it is the lowest for the I_3^- case.

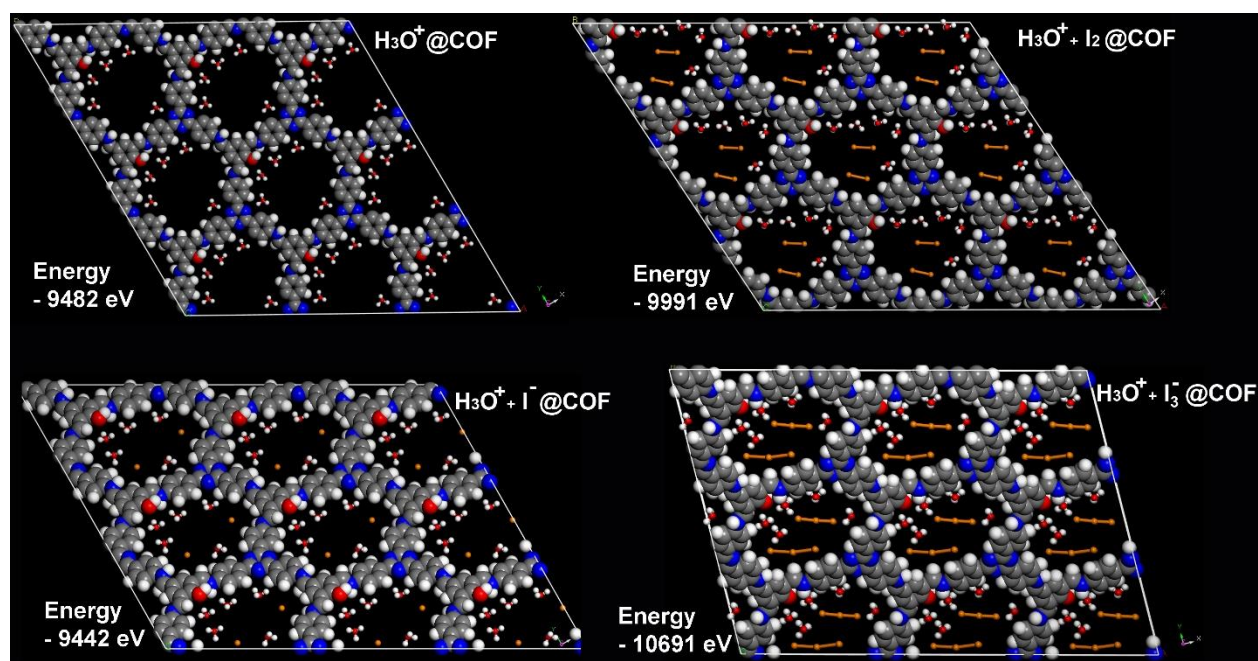


Figure A.2.53. Guest-included structures of the COF optimized using the Simulated Annealing routine based Monte-Carlo methods. The optimized structures shown here is obtained by subjecting the guest included COF to an isotropic external electric field of 0.05 eV/Å/e/unit-cell using the CASTEP routine. The structure with I_3^- ions shows the lowest energy and some of the I_3^- units are bent. Many of the H_3O^+ ions reside at distances favorable for interacting with the I_3^- . No unacceptable distances violating the Vander Waals constraints are found. Remark: The structures collapse when higher external fields are applied (RSC Adv., 2017, 7, 56676).

References:

- A.2.1.** P. Bhanja, S. K. Das, K. Bhunia, D. Pradhan, T. Hayashi, Y. Hijikata, S. Irle, A. Bhaumik, *ACS Sustainable Chem. Eng.* **2018**, 6, 202.^a
- A.2.1.** S. K. Das, K. Bhunia, A. Mallick, A. Pradhan, D. Pradhan, A. Bhaumik, *Microporous Mesoporous Mater.* **2018**, 266, 109.^a
- A.2.1.** S. Chandra, D. Roy Chowdhury, M. Addicoat, T. Heine, A. Paul, R. Banerjee, *Chem. Mater.* **2017**, 29, 2074.^a
- A.2.1.** Q. Xu, Y. Tang, L. Zhai, Q. Chen, D. Jiang, *Chem. Commun.* **2017**, 53, 11690.^a
- A.2.1.** Y. Han, Q. Zhang, N. Hu, X. Zhang, Y. Mai, J. Liu, X. Hua, H. Wei, *Chin. Chem. Lett.* **2017**, 28, 2269.^a
- A.2.1.** G. Kim, J. Yang, N. Nakashima, T. Shiraki, *Chem. Eur. J.* **2017**, 23, 17504.^a
- A.2.1.** P. Wang, Q. Wu, L. Han, S. Wang, S. Fang, Z. Zhang, S. Sun, *RSC Adv.* **2015**, 5, 27290.^a
- A.2.8.** S. Kandambeth, J. Jia, H. Wu, V. S. Kale, P. T. Parvatkar, J. Czaban-Jóźwiak, S. Zhou, X. Xu, Z. O. Ameer, E. Abou-Hamad, E. Abdul-Hamid, S. Osama, H. N. Alshareef, M. Eddaoudi, *Adv. Energy Mater.* **2020**, 10, 2001673.^c
- A.2.9.** S. Haldar, R. Kushwaha, R. Maity, R. Vaidhyanathan, *ACS Materials Lett.* **2019**, 1, 4, 490.^c

- A.2.10.** Y. Wu, D. Yan, Z. Zhang, M. M. Matsushita, K. Awaga, *ACS Appl. Mater. Interfaces* **2019**, *11*, 8, 7661.^a
- A.2.11.** A. Khayum M, V. Vijayakumar, S. Karak, S. Kandambeth, M. Bhadra, K. Suresh, N. Acharambath, S. Kurungot, R. Banerjee, *ACS Appl. Mater. Interfaces* **2018**, *10*, 28139.^c
- A.2.12.** A. Halder, M. Ghosh, A. Khayum M, S. Bera, M. Addicoat, H. S. Sasmal, S. Karak, S. Kurungot, R. Banerjee, *J. Am. Chem. Soc.* **2018**, *140*, 10941.^c
- A.2.13.** L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen, B. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 4920.^c
- A.2.14.** H. Li, D. Fu, X.-M. Zhang, *R. Soc. open sci.* **2018**, *5*, 171028.^c
- A.2.15.** D. Fu, H. Zhou, X. M. Zhang, G. Han, Y. Chang, H. Li, *ChemistrySelect* **2016**, *1*, 285.^c
- A.2.16.** R. Hou, M. Miao, Q. Wang, T. Yue, H. Liu, H. S. Park, K. Qi, B. Y. Xia, *Adv. Energy Mater.* **2019**, 1901892.^c
- A.2.17.** A. Singh, A. Chandra, *Sci. Rep.* **2016**, *6*, 25793.^c
- A.2.18.** J. Wu, H. Yu, L. Fan, G. Luo, J. Lin, M. Huang, *J. Mater. Chem.* **2012**, *22*, 19025.^a
- A.2.19.** K. Jayaramulu, D. P. Dubal, B. Nagar, V. Ranc, O. Tomanec, M. Petr, K. K. R. Datta, R. Zboril, P. Gómez-Romero, R. A. Fischer, *Adv. Mater.* **2018**, *30*, 1705789.^c

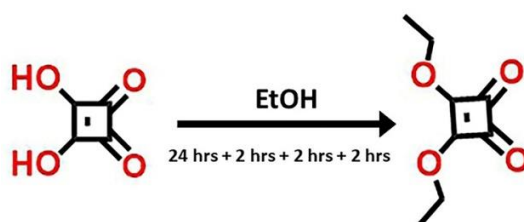
Note: Type of measurement set-up used in these studies have been classified in the reference list as follows: a = three-electrode set-up only, b = two-electrode device only and c = both (two and three-electrode set-up).

Synthesis of diethyl squarate:

This compound was synthesized following previously reported method with slight modification[#].

[#]Sopeña *et al.* *ACS Catal.* **2017**, 7, 3532–3539.

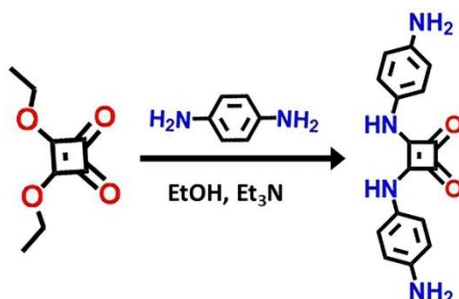
Squaric acid (5 g) was suspended in ethanol (70 mL) and stirred under reflux for 24 hours. The reaction mixture was cooled, and the solvent was removed with a rotatory evaporator. The white solid was redissolved in ethanol and brought to reflux for 2 hours. This step was repeated three times to obtain the complete conversion of squaric acid into diethyl squarate.

**Synthesis of the 3,4-bis((4-aminophenyl)amino)cyclobut-3-ene-1,2-dione:**

This compound was synthesized following previously reported method with slight modification[#].

[#]Li *et al.* *Chem. Commun.*, **2019**, 55, 5423–5426.

3,4-diethoxycyclobut-3-ene-1,2-dione (1.25 g, 7.35 mmol), benzene 1,4-diamine (2 g, 18.50 mmol) and triethylamine (10.24 mL) were dissolved in 70 mL ethanol. The mixture was stirred at room temperature for 24 hours. The resulting precipitate was collected by filtration and cleaned with plenty of ethanol and diethyl ether to yield the product as a beige/yellow.



Synthesis of the protected ligand 3,4-bis((4-((E)-benzylideneamino)phenyl)amino)cyclobut-3-ene-1,2-dione:

In a 15 mL Teflon liner, 3,4-bis((4-aminophenyl) amino) cyclobut-3-ene-1,2 -dione (249 mg, 1 mmol) was dissolved in 12 mL MeOH and 1 mL DMA. Then benzaldehyde (210 μ L) was added. After 15 minutes of stirring, 0.5 mL of glacial acetic acid was added to it. The resulting mixture was allowed to stir for 10 mins. Finally, it was kept at 100 $^{\circ}$ C for 24 hours. After that, the resulting precipitate was collected by filtration and washed with MeOH and then CH_2Cl_2 to yield the product as an off-white solid. ^1H NMR (400 MHz, DMSO) δ 9.99 (s, 1H), 8.67 (s, 1H), 7.94 (dd, J = 6.6, 3.0 Hz, 2H), 7.60 – 7.44 (m, 5H), 7.36 (d, J = 8.7 Hz, 2H).

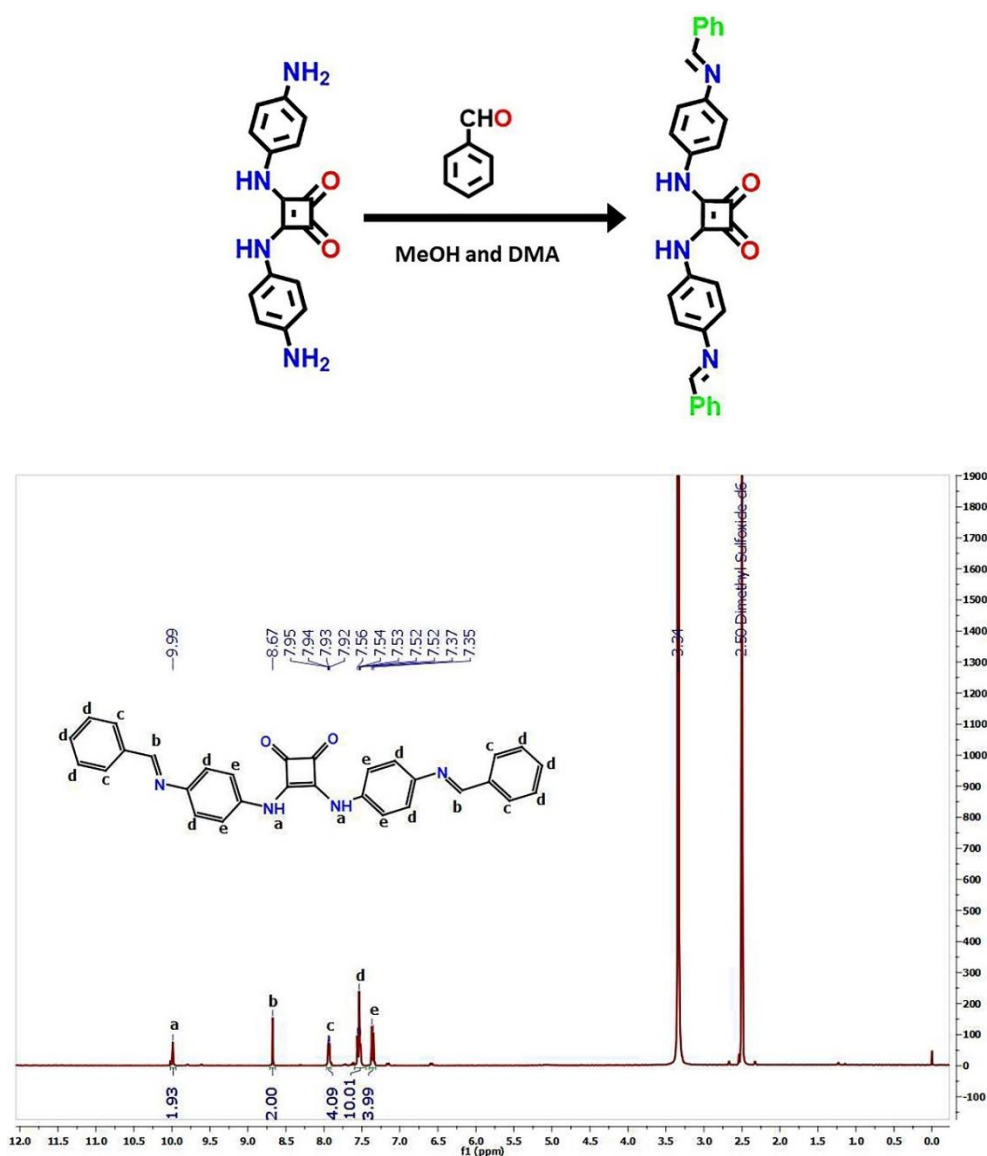


Figure A.3.1. ^1H NMR spectra of the protected ligand at 400 MHz. a,b,c,d, and e are the positions of the corresponding peaks obtained from the NMR data.

Table A.3.1. Reaction conditions that screened for COF synthesis.

Sr No.	SQM ligand (mg)	3-OH ligand (mg)	Solvent Conditions (ml)	Acid catalyst (ml)	Temperature	Crystallinity
1.	44.5	30	Mesitylene/Dioxane 2/2	6M AcOH 0.3	120°C, 72 hrs	No
2.	44.5	30	Mesitylene/ODCB/Ethanol 1.5/1/2	AcOH 0.3	120°C, 72 hrs	low
3.	44.5	30	Mesitylene/ODCB/DMA 2/2/0.5	6M AcOH 0.3	120°C, 72 hrs	Very low
4.	44.5	30	Mesitylene/ODCB/Ethanol 1.5/1/2	6M AcOH 0.3	90°C, 72 hrs	Very low
5.	44.5	30	Mesitylene/Dioxane 3/2	TFA 0.1	90°C, 72 hrs	No
6.	44.5	30	Mesitylene/ODCB/DMA 2/2/0.5	AcOH 0.3	90°C, 72 hrs	low
7.	44.5	30	Mesitylene/ODCB/DMA 2/1/0.5	TFA 0.2	120°C, 72 hrs	Very low
8.	Protected sqm 70	24	Mesitylene/ODCB/Ethanol 1.5/1/2	6M AcOH 0.5	120°C, 72 hrs	moderate

9.	Protected sqm 70	24	Mesitylene/ODCB/Ethanol 1.5/1/2	TFA 0.2	120°C, 72 hrs	low
10.	Protected sqm 70	24	Mesitylene/ODCB/Ethanol 1.5/1/2	AcOH 0.3	120°C, 72 hrs	Highly Crystalline

Table A.3.2. Atomic parameters for IISERP-COF22.

Atom	x/a	y/b	z/c
C1	0.56118	0.45264	0.5
C2	0.4963	0.43823	0.5
O3	0.31089	0.55999	0.5
C4	0.39166	0.62916	0.5
N5	0.48929	0.50905	0.5
C6	0.47023	0.46152	0.5
O7	0.39519	0.40188	0.5
O8	0.46211	0.34639	0.5
C9	0.66826	0.35083	0.5
C10	0.84324	0.38892	0.5
N11	0.80415	0.36091	0.5
O12	0.27287	0.68653	0.5
C13	0.25198	0.59554	0.5
N14	0.06795	0.52745	0.5
C15	0.53674	0.01323	0.5
N16	0.48326	0.96095	0.5
C17	0.51951	0.96672	0.5
C18	0.57359	0.00895	0.5
C19	0.55685	0.96409	0.5
O20	0.55718	0.9221	0.5
N21	0.38666	0.58532	0.5
C22	0.46545	0.52768	0.5
O23	0.73239	0.42347	0.5

N24	0.53436	0.46711	0.5
C25	0.12501	0.60475	0.5
C26	0.16866	0.62854	0.5
C27	0.18702	0.59817	0.5
N28	0.22667	0.61474	0.5
C29	0.10865	0.55263	0.5
C30	0.04244	0.4804	0.5
O31	0.74924	0.28375	0.5
C32	0.78055	0.37949	0.5
N33	0.96876	0.46335	0.5
C34	0.99819	0.4559	0.5
C35	0.04393	0.43376	0.5
C36	0.99942	0.41026	0.5
O37	0.96643	0.36526	0.5
O38	0.07872	0.43131	0.5
C39	0.39109	0.85054	0.5
C40	0.42047	0.90425	0.5
C41	0.47863	0.88144	0.5
C42	0.45128	0.82842	0.5
C43	0.41102	0.82137	0.5
N44	0.3936	0.77417	0.5
C45	0.46186	0.91411	0.5
O46	0.61396	0.26597	0.5
C47	0.66535	0.23337	0.5
N48	0.518	0.03891	0.5
C49	0.36449	0.64238	0.5
O50	0.41247	0.72393	0.5
C51	0.37248	0.68976	0.5
C52	0.34375	0.70346	0.5
C53	0.30102	0.67255	0.5
C54	0.29083	0.62337	0.5
C55	0.3202	0.60695	0.5
C56	0.4341	0.41163	0.5
C57	0.45984	0.38817	0.5

C58	0.60332	0.49124	0.5
C59	0.63519	0.47839	0.5
C60	0.62185	0.42591	0.5
C61	0.57953	0.3885	0.5
C62	0.54662	0.40021	0.5
N63	0.65115	0.41334	0.5
C64	0.64324	0.36707	0.5
C65	0.65456	0.2983	0.5
C66	0.68141	0.28052	0.5
C67	0.72565	0.30481	0.5
C68	0.74105	0.35423	0.5
C69	0.71414	0.37397	0.5
C70	0.86461	0.36202	0.5
C71	0.9095	0.38834	0.5
C72	0.93027	0.44117	0.5
C73	0.90814	0.46718	0.5
C74	0.86374	0.44131	0.5
N75	0.62729	0.21469	0.5
C76	0.48084	0.57898	0.5
C77	0.45428	0.60084	0.5
C78	0.41189	0.56862	0.5
C79	0.39492	0.51836	0.5
C80	0.42209	0.49825	0.5
C81	0.35467	0.74926	0.5
C82	0.59753	0.17143	0.5
C83	0.61488	0.13952	0.5
C84	0.58276	0.08794	0.5
C85	0.54333	0.08488	0.5
C86	0.52529	0.11617	0.5
C87	0.55831	01-Jun	0.5
C88	0.17053	0.54628	0.5
C89	0.12621	0.52274	0.5
O90	0.61264	0.04498	0.5

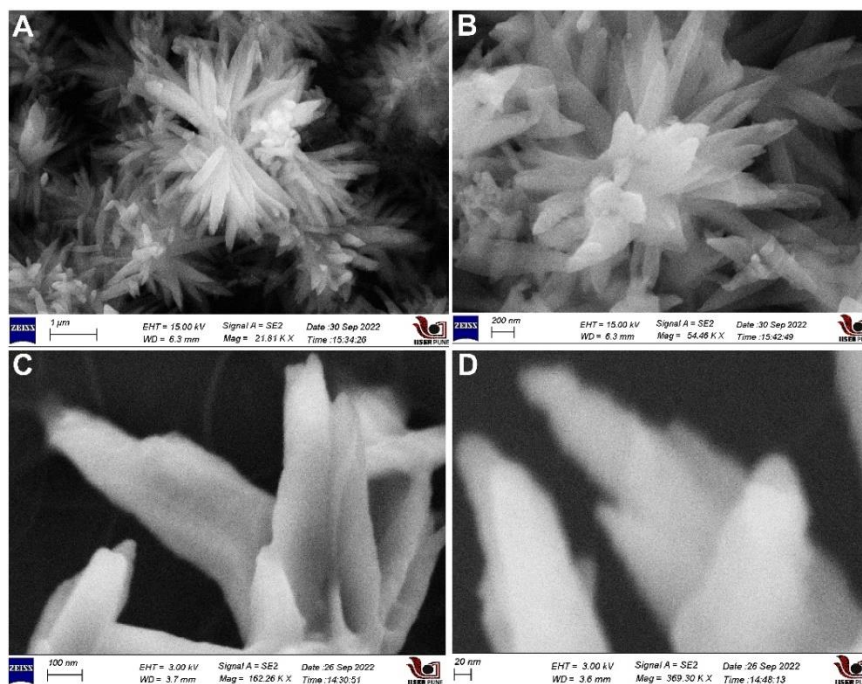
Morphological studies:

Figure A.3.2. FESEM images of IISERP-COF22 at different resolutions. It shows flaky The COF shows aloe vera flowers-like morphology. At the lower resolution, a fluffy dendritic morphology can be seen. Whereas at higher resolution, the presence of sheet showing petal-like arrangement can be seen.

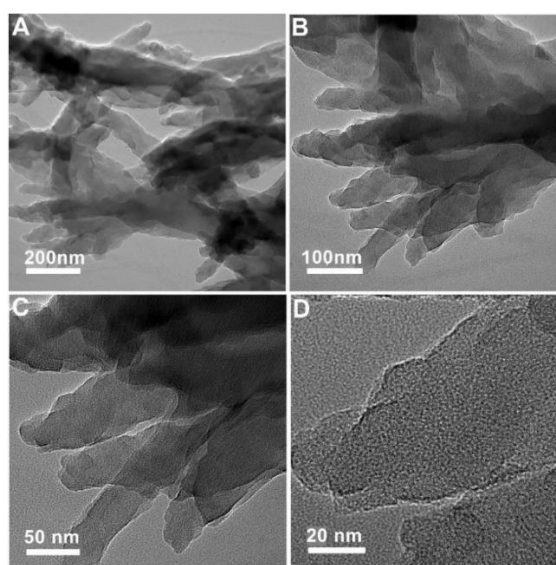


Figure A.3.3. HRTEM images of the IISERP-COF22 under different magnifications showing the aggregates formed by the stacking of many hexagonal sheets. At 20nm, presence of uniform micropores on the surface can be observed.

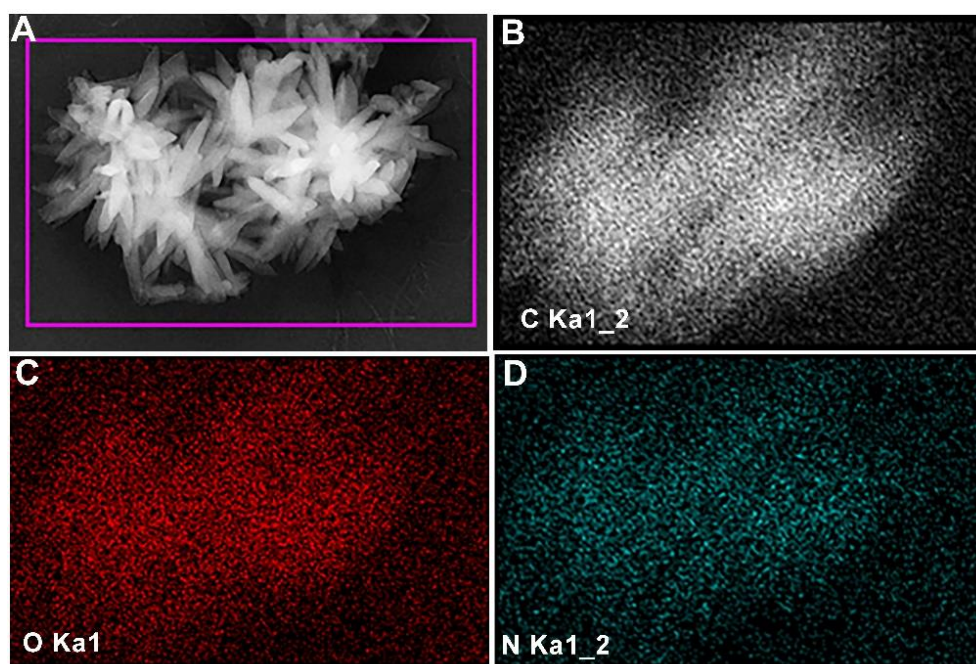


Figure A.3.4. The elemental mapping reveals the homogeneous distribution of constituents in the as made IISERP-COF22.

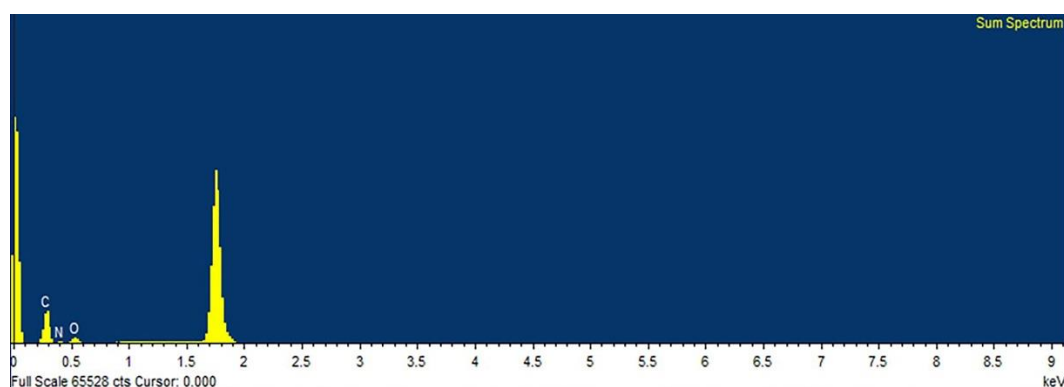


Figure A.3.5. The EDAX assisted full-scale spectrum of as-made IISERP-COF22 shows the elementals present in the sample.

Electrochemical Measurements

Three electrode measurements:

The COF (16 mg; 80%) and Super P carbon (3 mg; 15%) were mixed in a mortar pestle. It was ground thoroughly to make a homogeneous mixture, then Nafion solution (1 mg; 5%), and 1.5 mL ethanol was added and ground to make a homogenous slurry. This slurry was kept at 60 °C to vaporize the ethanol.

Then the composite material was reground to fine-power. About 1 mg of the composite material was weighed using a balance (Sartorius Quintix35-1S semi microbalance) with a precision of 0.01 mg. Composite materials were dispersed in 0.5 mL ethanol in an Eppendorf and sonicated for 2 hrs. It was drop-casted on a 1cm x 1cm area of Toray paper of size 1cm x 5cm and dried. The excess area of the Toray paper was covered with scotch tape so that only the coated area would be exposed to the solution. Ag/AgCl and a large Platinum flag were used as the reference and the counter electrodes. A potential window of -1 to 0.9 V was employed.

Note: Additional care was taken for storing ZnI_2 . In fact, we have observed that if not done with sufficient care, the hydrolysis and oxidation type of attacks by moisture results in a yellow-colored cloudy solution when ZnI_2 is employed. Typically, this generates Zn(OH)_2 and I_2 , which can interfere with the UV-Vis spectra as well as electrochemical measurements obtained from such media. Knowing this, we had taken all the preventive measures such as storing the solutions/salts in tightly sealed desiccators, used freshly prepared ZnI_2 solution for all measurements and during three electrode measurements, we covered the setup with Aluminium foil to avoid photodegradation.

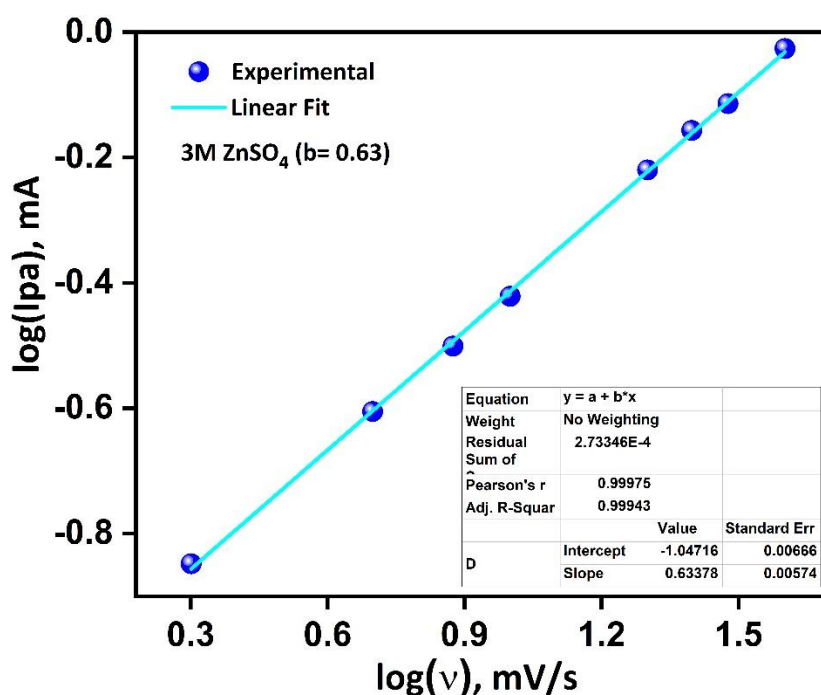


Figure A.3.6. A plot of the $\log(I_{pa})$ vs. $\log(v)$ measured in 3M ZnSO_4 electrolyte. Where I_{pa} is anodic peak current and v is scan rate employed for the cyclic voltammograms measured in three-electrode assembly using composite-coated Toray paper as the working electrode.

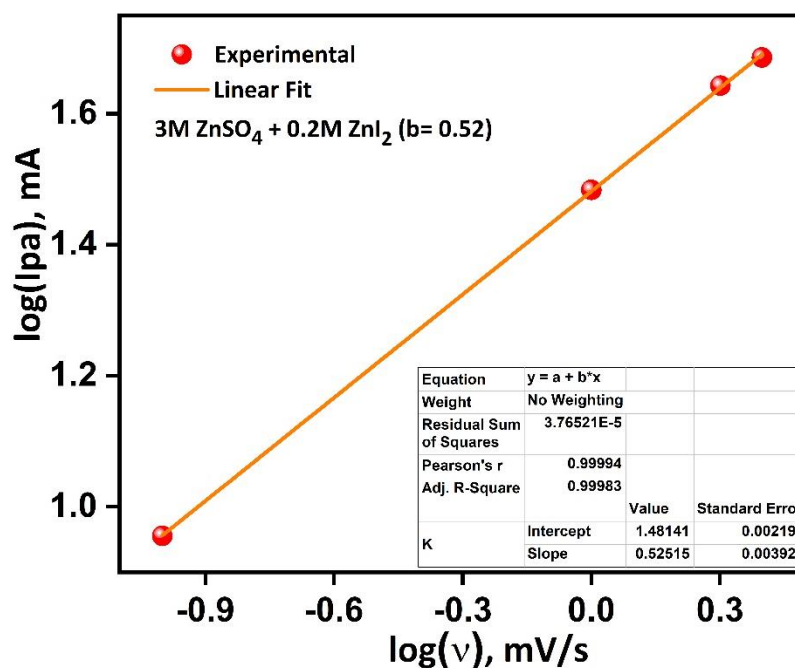


Figure A.3.7. A plot of the $\log(I_{pa})$ vs. $\log(v)$ measured in 3M $ZnSO_4 + 0.2M ZnI_2$ electrolyte. Where I_{pa} is anodic peak current and v is scan rate employed for the cyclic voltammograms measured in three-electrode assembly using composite-coated Toray paper as the working electrode.

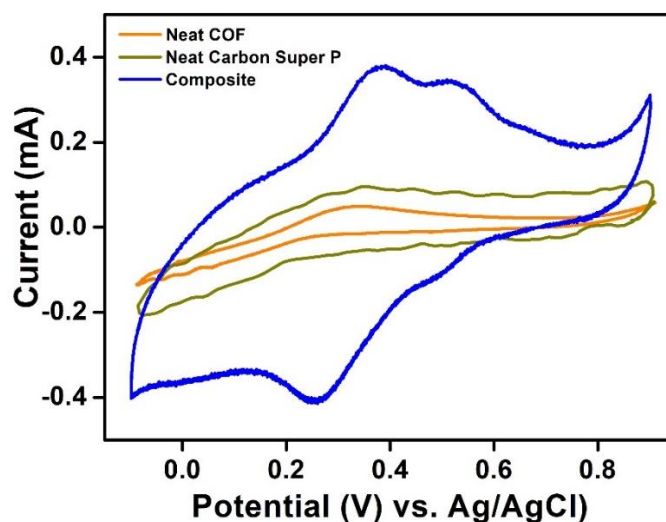


Figure A.3.8. All CVs shown in this figure have been measured in a three-electrode assembly, the plots of the neat COF versus super P carbon versus the composite measured using 3M $ZnSO_4$ as an electrolyte @ 2 mV/s scan rate with ~1 mg loading of materials, using Toray carbon paper as working electrode.

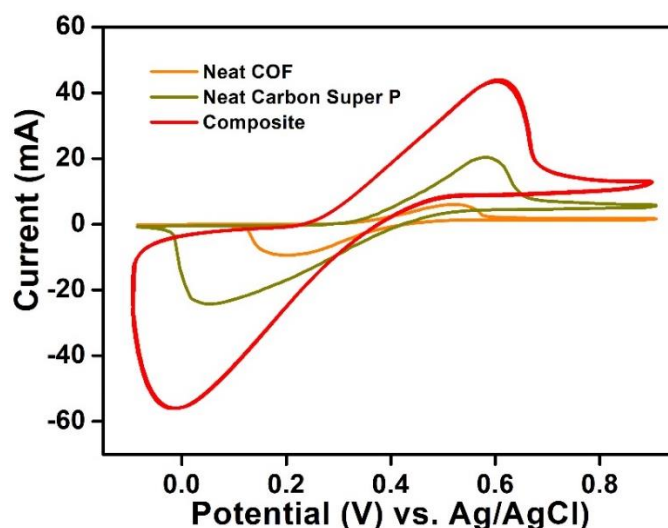


Figure A.3.9. All CVs shown in this figure have been measured in a three-electrode assembly, the plots of the neat COF versus super P carbon versus the composite measured using 3M ZnSO_4 + 0.2M ZnI_2 as an electrolyte @ 2 mV/s scan rate with ~1 mg loading of materials, using Toray carbon paper as working electrode.

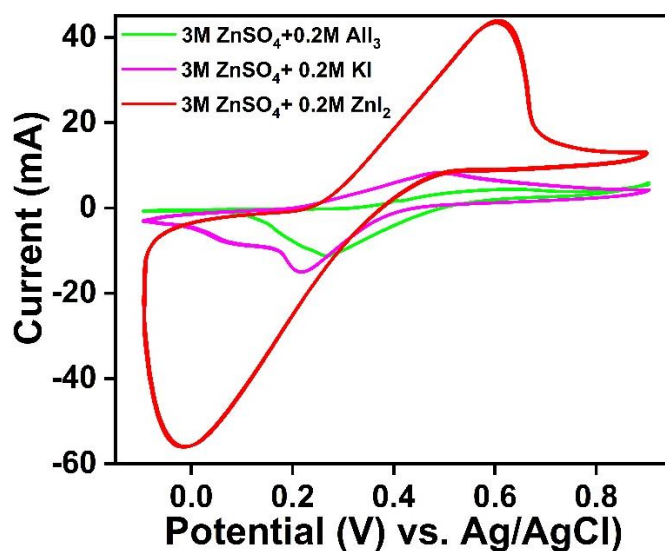


Figure A.3.10. All CVs shown in this figure have been measured in a three-electrode assembly, the plots of the neat COF versus super P carbon versus the composite measured using 3M ZnSO_4 + 0.2M AlI_3 , 3M ZnSO_4 + 0.2M KI and 3M ZnSO_4 + 0.2M ZnI_2 as an electrolyte @2 mV/s scan rate with ~1 mg loading of materials, using Toray carbon paper as working electrode.

Note: All these CV profile and currents were obtained reproducibly across different batch of samples.

Electrochemical measurements in the coin cell assembly:

A coin cell assembly was fabricated employing COF-coated carbon cloth as a cathode and Zn foil as an anode. The COF (50 mg; 80%), Super P carbon (15 mg; 15%), and 5% of Nafion binder (5mg) were added to the mortar pestle. After that, it was crushed thoroughly to make it homogeneous, and a good amount of ethanol was added. Homogenous slurry was made by using mortar-pestle. It was drop-casted to the area of 8cm x 8cm of carbon cloth. The traces left in the mortar were redispersed in the ethanol and drop-casted and dried. Finally, we obtained a loading of $\sim 1 \text{ mg cm}^{-2}$ of composite. A piece of metallic Zn foil was cleaned with diluted H_2SO_4 and ethanol to remove the surface oxide from the Zn sheet. Finally, a pre-soaked (3M ZnSO_4 and 3M $\text{ZnSO}_4 + 0.2\text{M ZnI}_2$) cellulose separator was sandwiched between the cathode and anode, assembled in the CR2032 coin cell. We represent this assembly as Zn//COF coin cell.

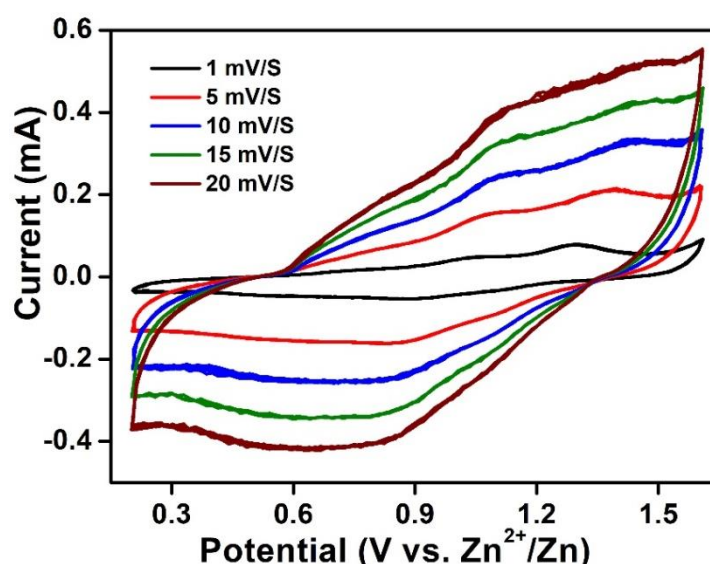


Figure A.3.11. CVs measured on a Zn//COF coin cell, fabricated using 3M ZnSO_4 as an electrolyte at different scan rates.

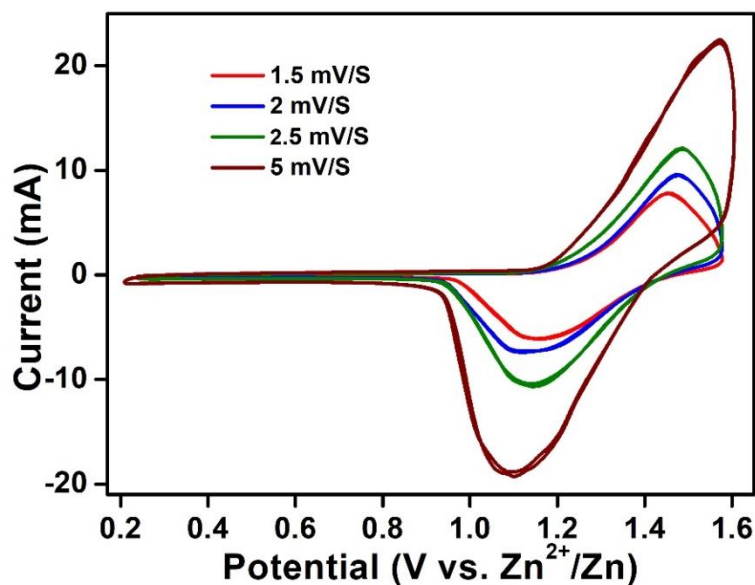


Figure A.3.12. CVs measured on a Zn//COF coin cell, fabricated using 3M ZnSO_4 + 0.2M ZnI_2 as an electrolyte at different scan rates.



Figure A.3.13. The images show the condition of the anode, cathode, and separator of our of Zn//COF coin cell, fabricated using 3M ZnSO_4 + 0.2M ZnI_2 as an electrolyte after 6000 cycles of charge-discharge measurements.

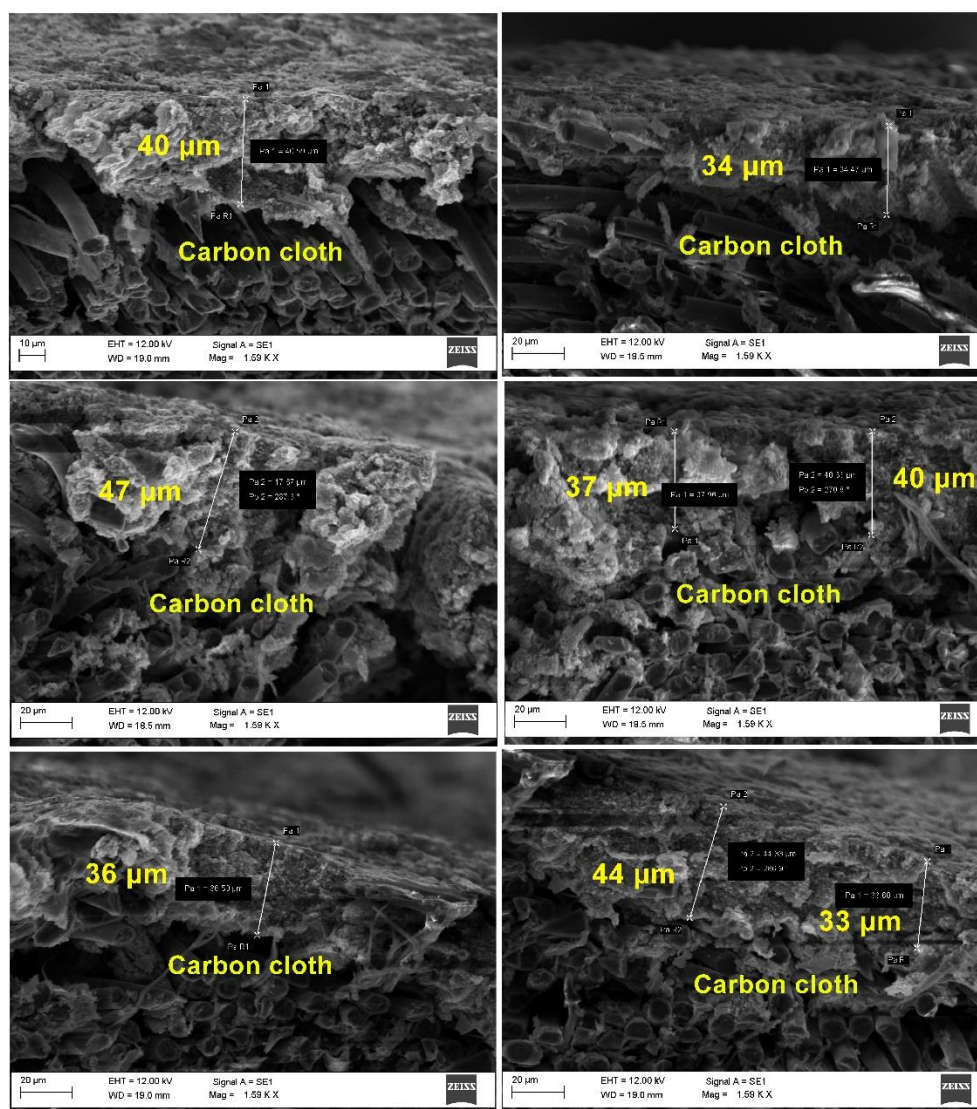


Figure A.3.14. SEM images show the thickness of IISERP-COF22 coated on the electrode through cross-section. It has been found that thickness varies from 30 to 50 microns. The measurements were carried out Carl ZeissEVO LS 10 Environmental Scanning Electron Microscope (ESEM).

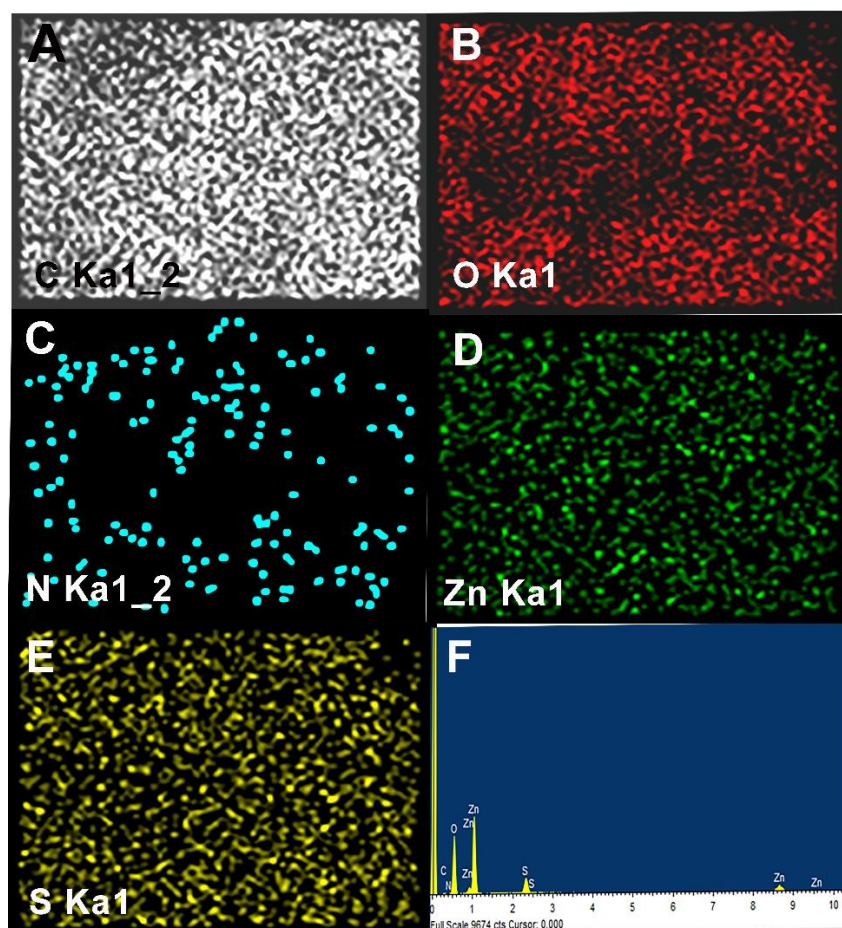


Figure A.3.15. The elemental mapping reveals the homogeneous distribution of Carbon, Nitrogen, Oxygen, Zinc, and Sulphur of material extracted from and washed from a discharged coin cell, fabricated using 3M ZnSO_4 as an electrolyte.

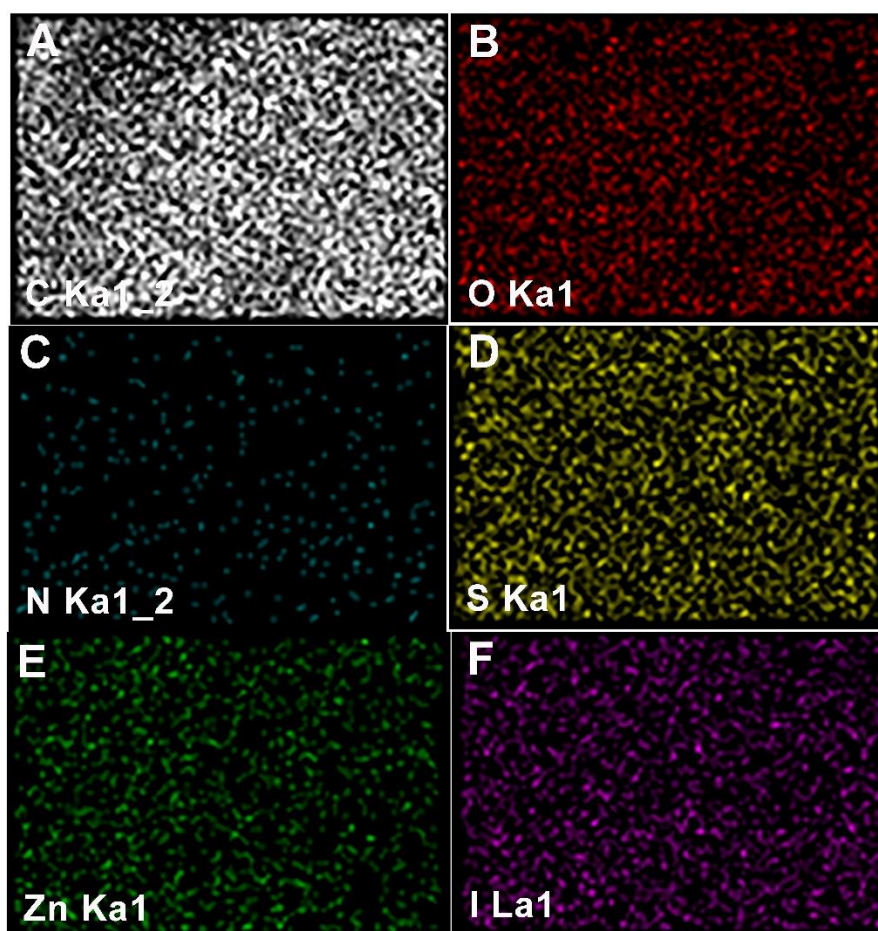


Figure A.3.16. The elemental mapping reveals the homogeneous distribution of Carbon, Nitrogen, Oxygen, Zinc, Iodine, and Sulphur of material extracted from and washed from a discharged coin cell, fabricated using 3M ZnSO_4 + 0.2M ZnI_2 as an electrolyte.

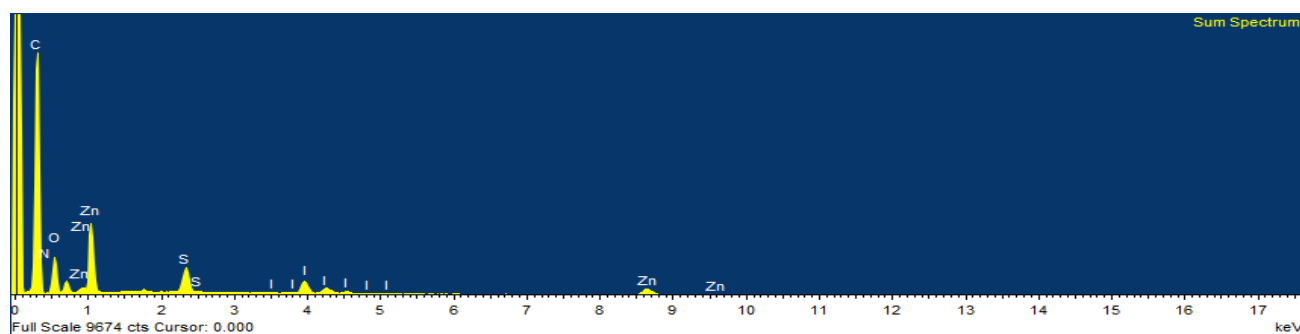


Figure A.3.17. The EDAX-assisted full-scale spectrum of material extracted from and washed from discharged coin cell, fabricated using 3M ZnSO_4 + 0.2M ZnI_2 as an electrolyte, shows the elementals present in the sample.

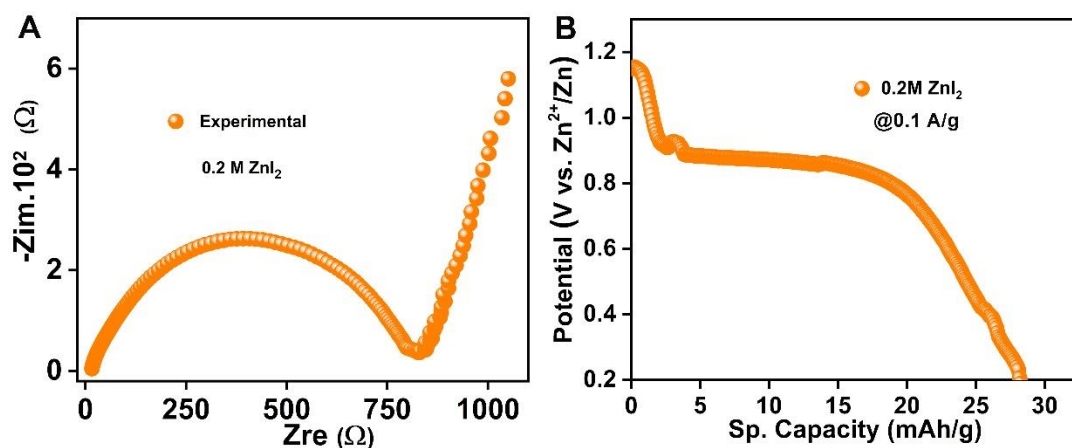


Figure A.3.18. (A) The impedance analysis of Zn//COF coin cell fabricated using 0.2M ZnI_2 (aq.). (B) Galvanostatic discharge curves at 0.1 A/g of Zn//COF coin cell fabricated using 0.2M ZnI_2 (aq.). Note: Due to the insufficient number of ions in the case of 0.2M ZnI_2 (800 Ω) the charge transfer resistance is even much higher than the obtained charge transfer resistance in the case of 3M $ZnSO_4$ (325 Ω) and 3M $ZnSO_4$ + 0.2M ZnI_2 (21 Ω). The specific capacity obtained 28 mAh/g @0.1 A/g, much lower than the specific capacity compared to 3M $ZnSO_4$ (208 mAh/g @1.5 A/g) and 3M $ZnSO_4$ + 0.2M ZnI_2 (690 mAh/g @1.5 A/g).

Calculation of Zn^{2+} and I_3^- ions concentration in the COF from the specific capacity:

$$Q = I \cdot t, 1\text{mA} = 10^{-3} \text{ A}, 1\text{hr} = 60 \cdot 60 \text{ sec}$$

$$1 \text{ mAh} = 10^{-3} \text{ A} \cdot 60 \cdot 60 \text{ sec} = 3.6 \text{ C}$$

$$1 \text{ electron carries } 1.6 \cdot 10^{-19} \text{ C of charge}$$

Thus, 1 C charge comes from $1/1.6 \cdot 10^{-19}$ no. of electrons e.g, $6.25 \cdot 10^{18}$ electrons or charge.

$$\text{Similarly, } 3.6 \text{ C} = 3.6 \cdot 6.25 \cdot 10^{18} = 2.25 \cdot 10^{19} \text{ number of electrons or charge.}$$

Here, for the COF-based coin-cells, if we observed a specific capacity of '690' mAh/g in the potential region of 0.2 – 1.6 Volt.

$$\text{It would yield the number of } \text{Zn}^{2+} \text{ ion and } \text{I}_3^- = (690 \cdot 2.25 \cdot 10^{19})/3 = (517.5 \cdot 10^{19})$$

Thus, the specific capacity of '690' mAh/g is realized from no. of Zn^{2+} and I_3^- ions (assuming they are the sole charge carriers).

If the calculated molecular weight of the COFs is '4780' g/mol. The weight for the unit cell of the COF

$$\text{is } 4780 / (6.023 \cdot 10^{23}) \text{ g.}$$

Considering that for 1g of the COF, the number of Zn^{2+} and I_3^- ions calculated is $517.5 \cdot 10^{19}$

$$\Rightarrow \text{number of } \text{Zn}^{2+} \text{ and } \text{I}_3^- \text{ per unit cell is calculated as: } (517.5 \cdot 10^{19} \cdot 4780) / (6.023 \cdot 10^{23}) = 41.07 \text{ total charge carriers.}$$

As Zn^{2+} and I_3^- are the sole charge carriers.

Therefore, for charge neutrality, for every Zn^{2+} , there will be 2 I_3^-

$$\text{Ratio of } \text{Zn}^{2+} \text{ and } \text{I}_3^- = 1:2$$

Therefore, the contribution of the respective ions can be calculated as:

$$3x = 41 \Rightarrow x = 13.6$$

$$\text{Total No. of } \text{Zn}^{2+} \text{ ions interacting per unit cell} \Rightarrow x \approx 13$$

$$\text{Total No. } \text{I}_3^- \text{ of ions interacting per unit cell} \Rightarrow 13.6 \cdot 2 \approx 27$$

Fabrication of flexible Zn ion battery

A flexible Zn//COF battery was fabricated using COF-coated carbon cloth as cathode and Zn foil as an anode. The COF (50 mg; 80%), Super P carbon (15 mg; 15%), and 5% of Nafion binder (5mg) were added to the mortar pestle. It was crushed thoroughly to make it homogeneous after that, and a good amount of ethanol was added. This slurry was kept at 80 °C to evaporate the ethanol. Then the composite material was scratched and ground. The fine-powered composite material of 1 mg was measured through a balance (Sartorius Quintix35-1S semi-microbalance) with a precision of 0.01 mg, kept in Eppendorf dispersed in 0.5 mL ethanol and sonicated for 2 hrs. It was drop-casted to an area of 1cm x 1cm of carbon cloth (cloth's entire dimension: 1cm x 4cm) and dried. A piece of metallic Zn foil (1cm x 4cm) was cleaned with diluted H_2SO_4 and ethanol to remove the surface oxide from the Zn sheet. Finally, a pre-soaked (3M ZnSO_4 and 3M ZnSO_4 + 0.2M ZnI_2) cellulose separator was sandwiched between the cathode and anode and assembled as a flexible Zn//COF battery.



Figure A.3.19. Optical images of the flexible Zn ion battery under different flexible angles.



Figure A.3.20. The images show that our flexible Zn ion batteries are able to power 3LEDs (traffic LEDs).

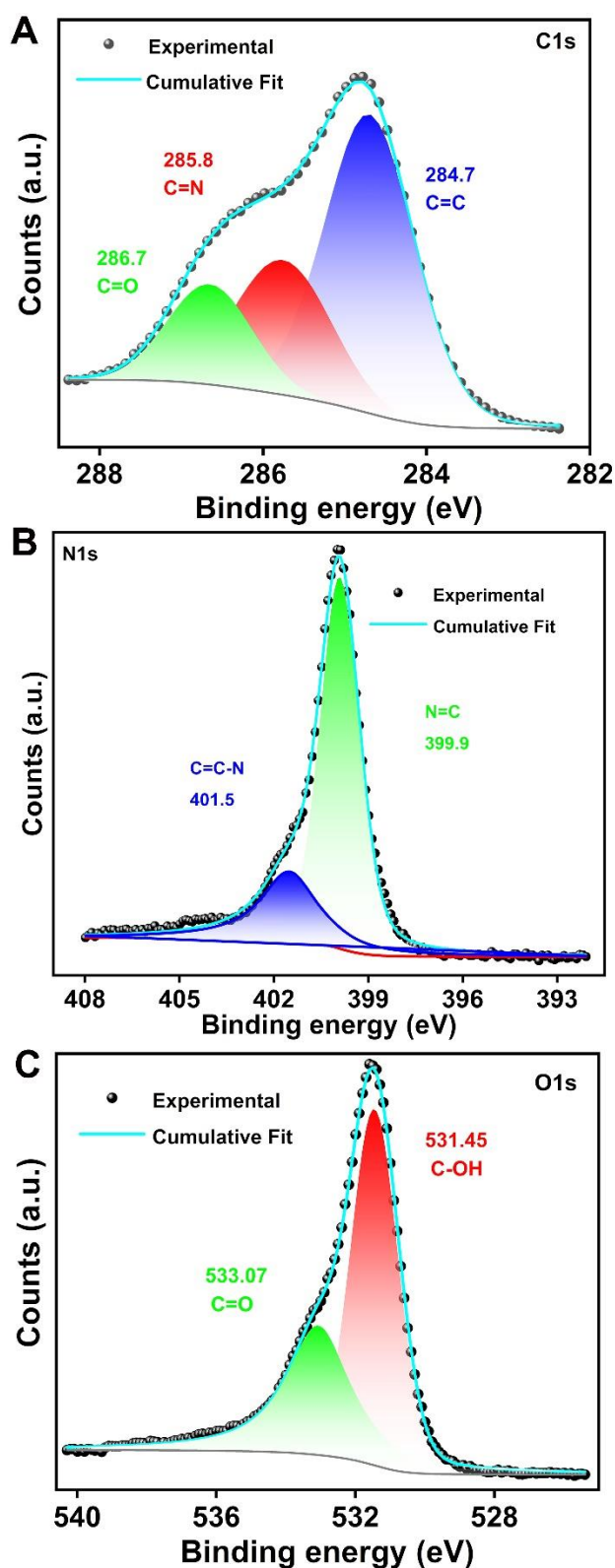
XPS of the as-made COF:

Figure A.3.21. X-ray Photoelectron Spectroscopy (XPS) spectra of IISERP-COF22.

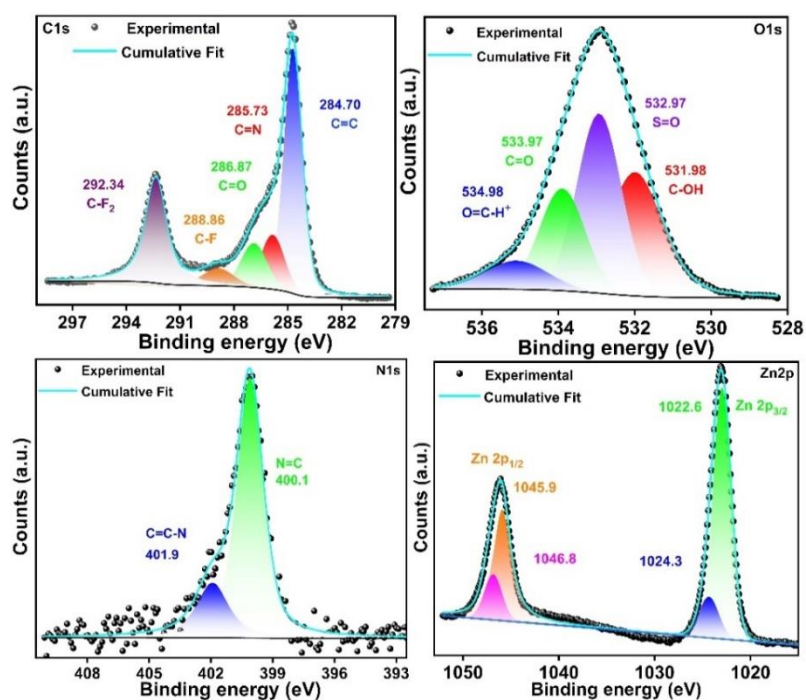
XPS of the COF discharged at 0.2 V in only ZnSO₄ electrolyte:

Figure A.3.22. X-ray Photoelectron Spectroscopy (XPS) collected from the cathode of Zn//COF coin cell discharged at 0.2V, fabricated using 3M ZnSO₄ as an electrolyte.

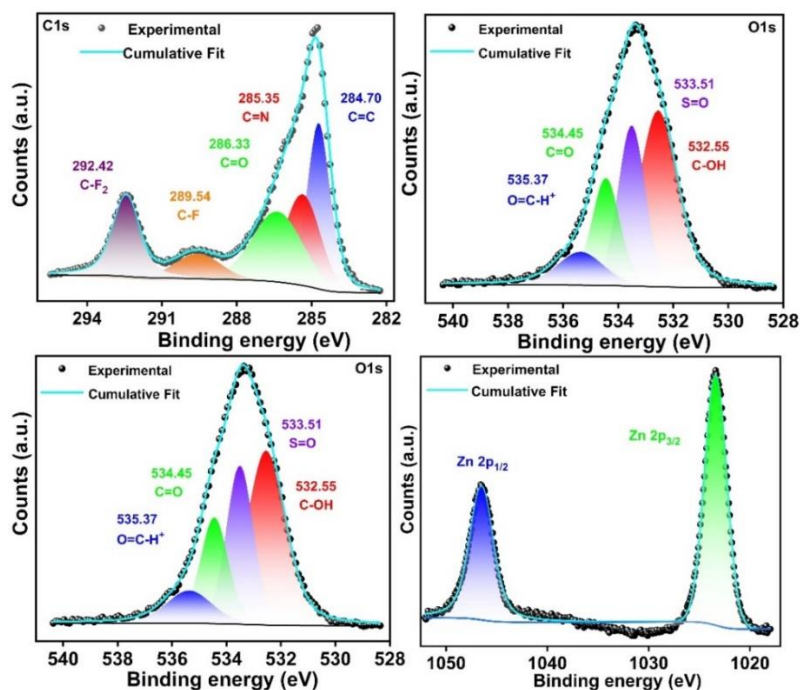
XPS of the COF charged at 1.5 V in only ZnSO₄ electrolyte:

Figure A.3.23. X-ray Photoelectron Spectroscopy (XPS) collected from the cathode of Zn//COF coin cell charged at 1.5 V, fabricated using 3M ZnSO₄ as an electrolyte.

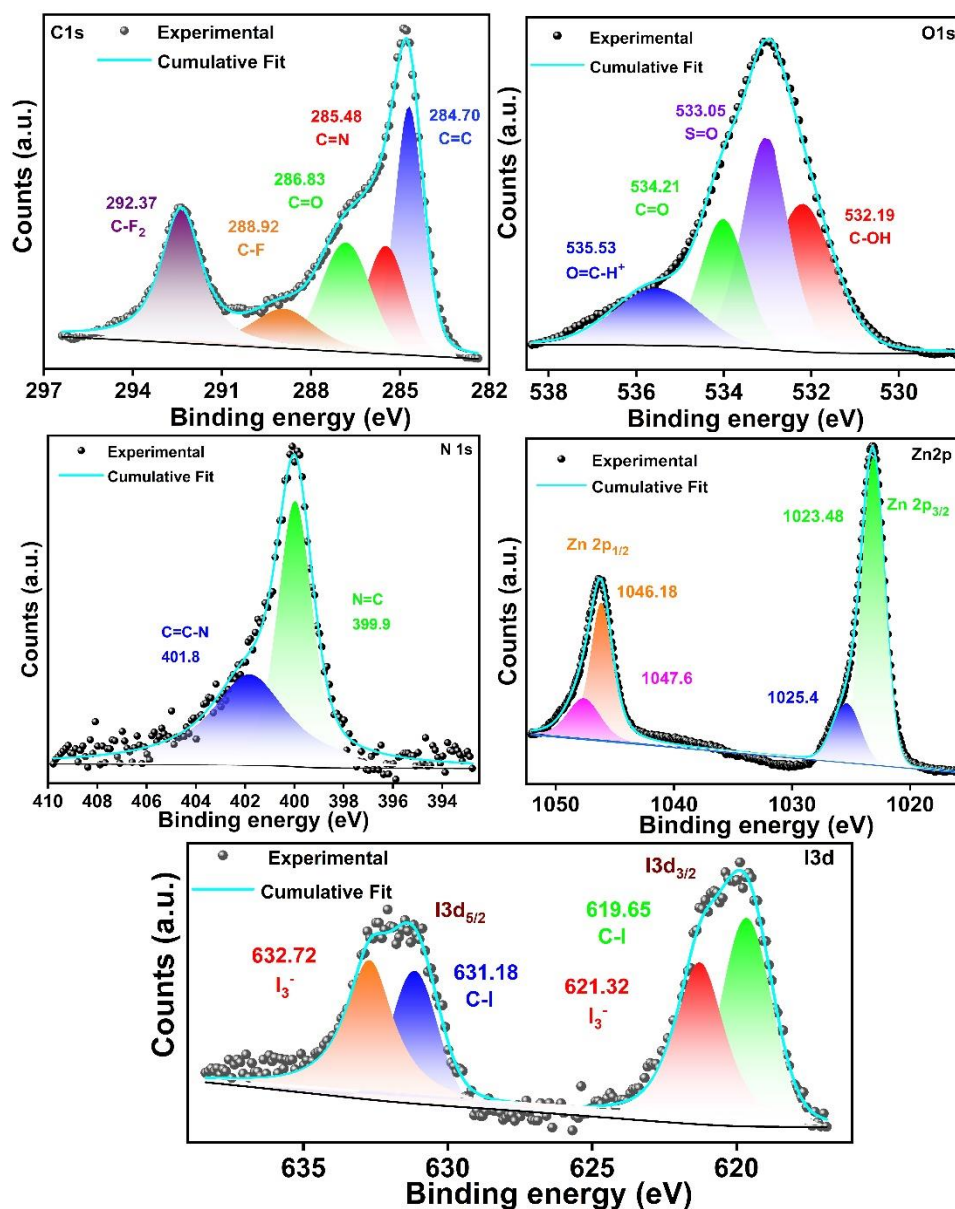
XPS of the COF discharged at 0.2 V in redox electrolyte ($\text{ZnSO}_4 + \text{ZnI}_2$):

Figure A.3.24. X-ray Photoelectron Spectroscopy (XPS) collected from the cathode of Zn//COF coin cell discharged at 0.2V, fabricated using 3M $\text{ZnSO}_4 + 0.2\text{M}$ ZnI_2 as an electrolyte. The electrode isolated from the charged coin-cell was removed in the same state, and washed with methanol before being subjected to the XPS analysis.

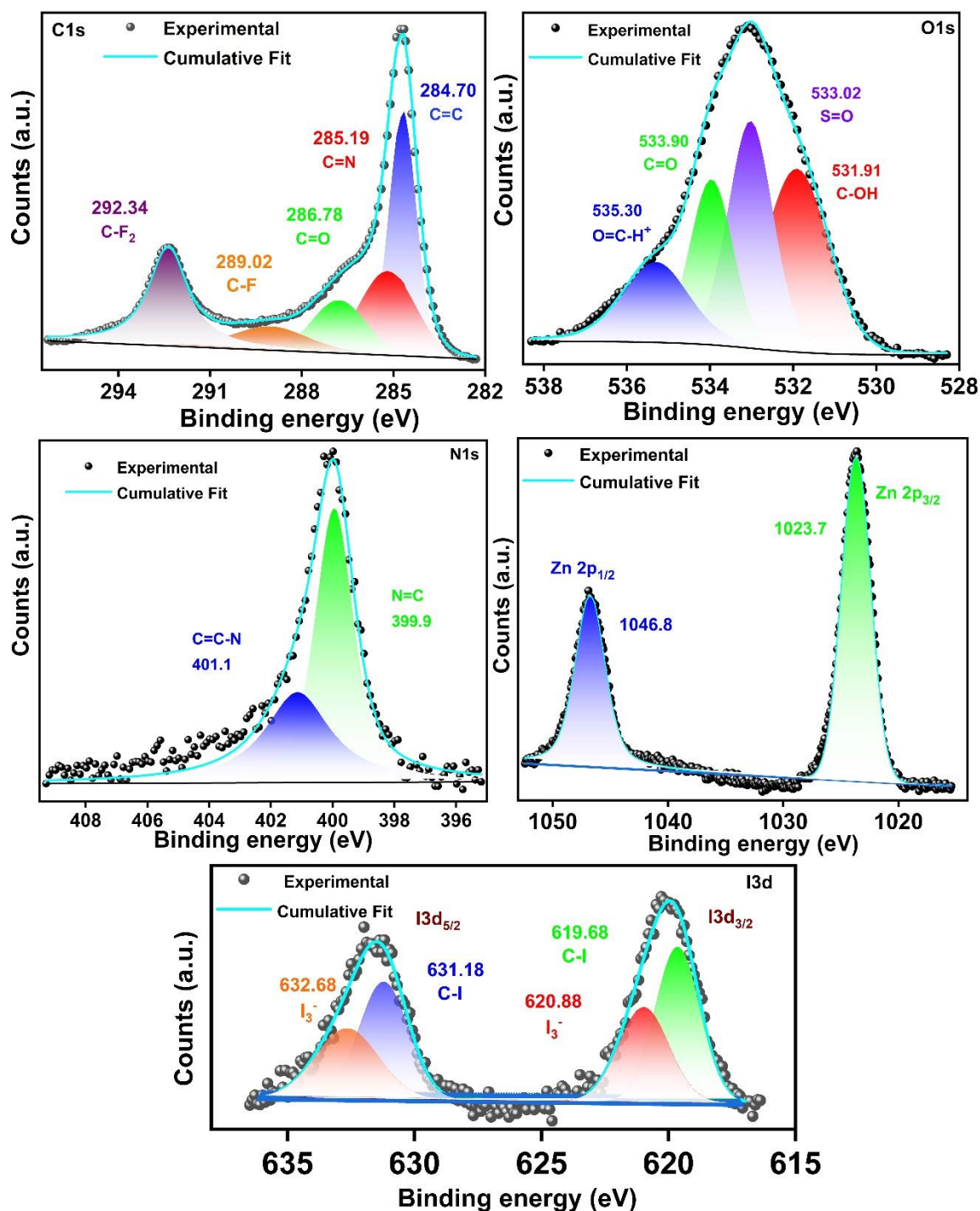
XPS of the COF charged at 1.5 V in redox electrolyte ($\text{ZnSO}_4 + \text{ZnI}_2$):

Figure A.3.25. X-ray Photoelectron Spectroscopy (XPS) collected from the cathode of Zn//COF coin cell charged at 1.5 V, fabricated using 3M $\text{ZnSO}_4 + 0.2\text{M}$ ZnI_2 as an electrolyte. The electrode isolated from the charged coin-cell was removed in the same state, and washed with methanol before being subjected to the XPS analysis. Note: Though the XPS signal is observed for iodide in samples extracted in both charged and discharged state, the relative intensity of the peaks for the charged state is much higher than that of the discharged. This explains that not all the stored charge is discharged.

Which agrees with the gradual decrease of specific capacity with cycles (Figure 3.12.H, Chapter 3).

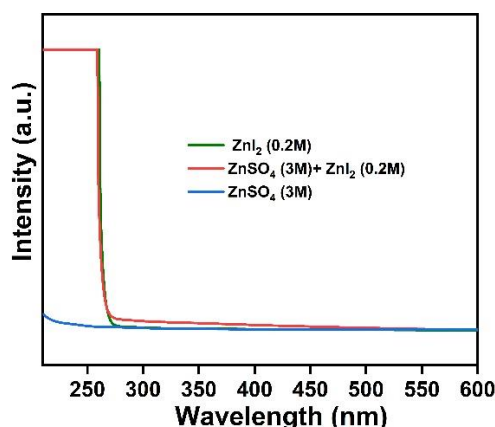


Figure A.3.26. Comparative UV-Vis spectra of 0.2M ZnI_2 (aq.), 3M ZnSO_4 (aq.) + 0.2M ZnI_2 (aq.) and 3M ZnSO_4 (aq.).

In situ spectro-electrochemistry:

Experimental Technique: First, the UV-Visible spectra of the 3M ZnSO_4 and 3M ZnSO_4 + 0.2M ZnI_2 electrolyte solution were taken as the two separate baselines. A dispersion of the IISERP-COF22 in ethanol was drop-casted on an ITO plate and dried. This COF-coated ITO plate was dipped into a cuvette filled with the electrolyte solution. The UV-Visible spectra of COF, taken in the presence of electrolyte solution (where the baselines were already corrected with 3M ZnSO_4 and 3M ZnSO_4 + 0.2M ZnI_2 electrolyte solution). Inside the UV cuvette, a typical three-electrode setup was built (similar to three electrode battery measurements) and connected to the ocean optics instrument to in situ monitor the change of the spectra. Then a chrono-amperometry measurement was carried out (at 0.8 V) up to 2 hours with the help of the CH instrument charge-discharge analyzer, and the UV-visible spectra were recorded.

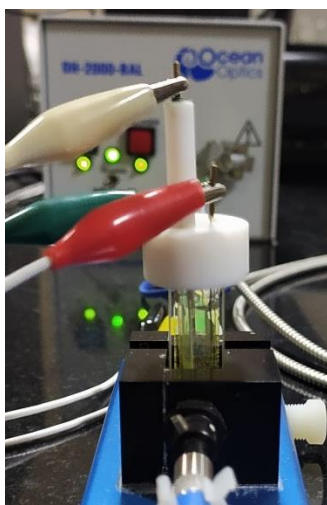


Figure A.3.27. The typical set-up of insitu spectro-electrochemistry.

Solid state UV-Vis:

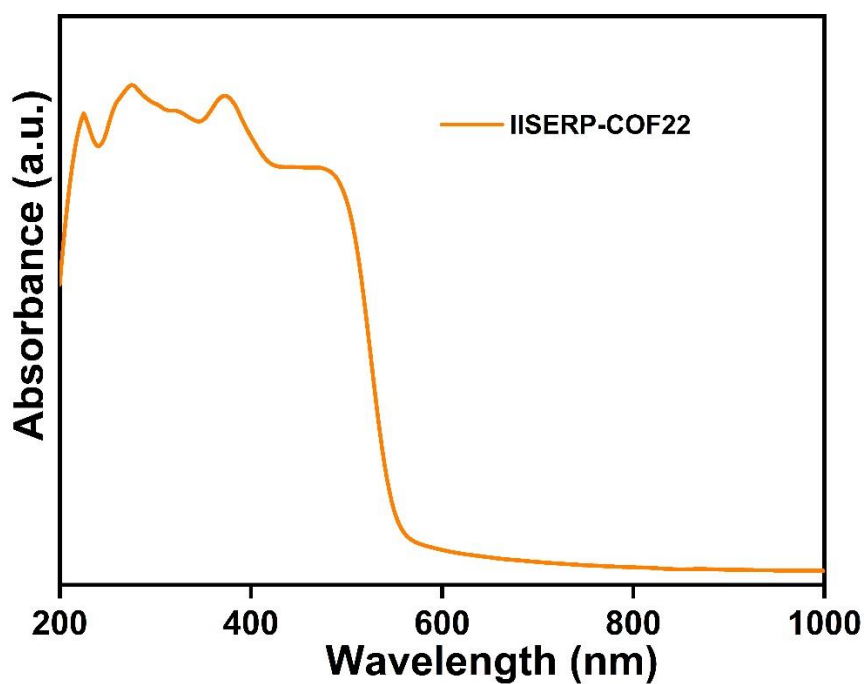


Figure A.3.28. The solid-state UV-Vis of as made IISERP-COF22.

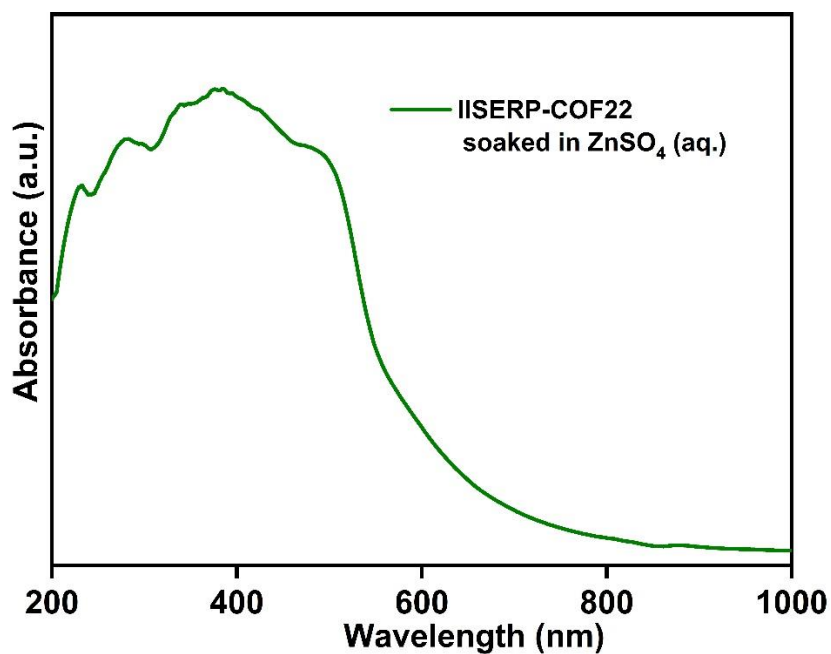


Figure A.3.29. The solid-state UV-Vis of IISERP-COF22 soaked in 3M ZnSO₄. The material was filtered, washed with MeOH dried in hot oven at 80 °C.

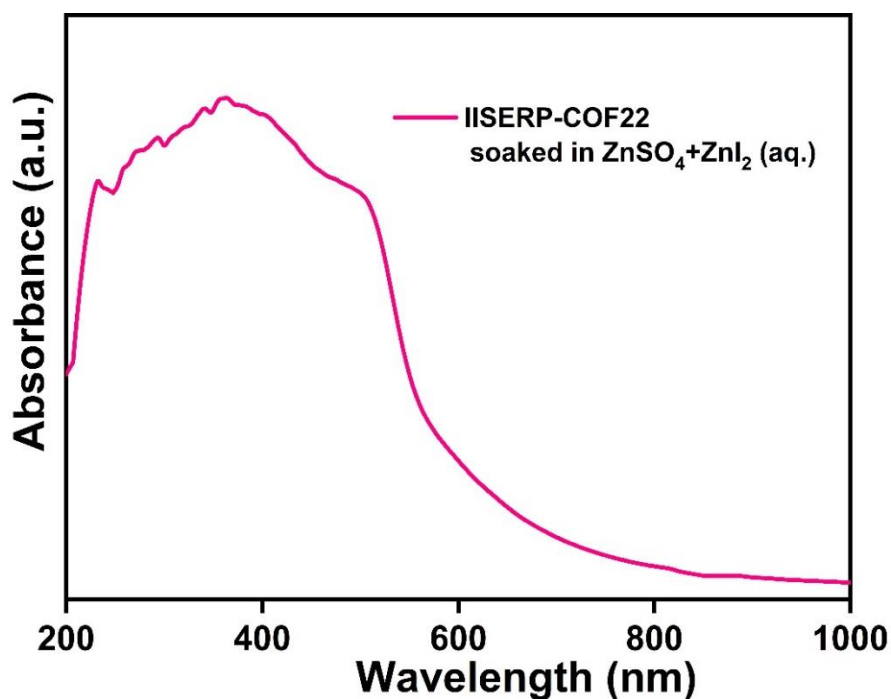


Figure A.3.30. The solid-state UV-Vis of IISERP-COF22 soaked in 3M $\text{ZnSO}_4 + 0.2\text{M}$ ZnI_2 . The material was filtered, washed with MeOH dried in hot oven at 80°C .

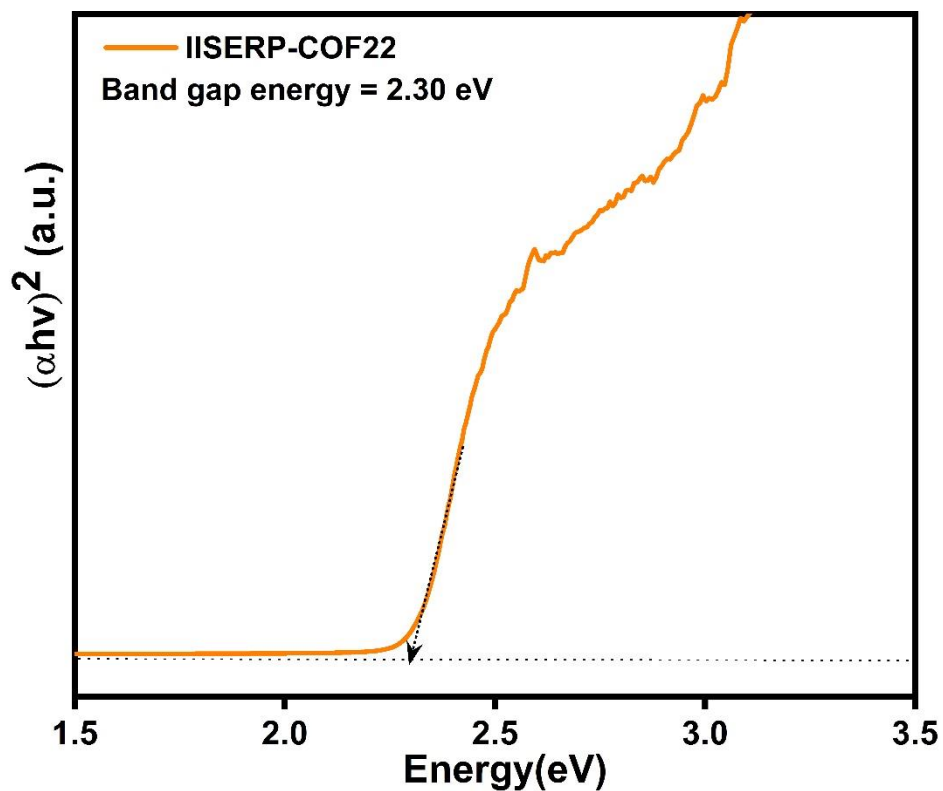


Figure A.3.31. Tauc plot to obtain the band gap of the as-made IISERP-COF22 using solid-state UV-Vis spectra.

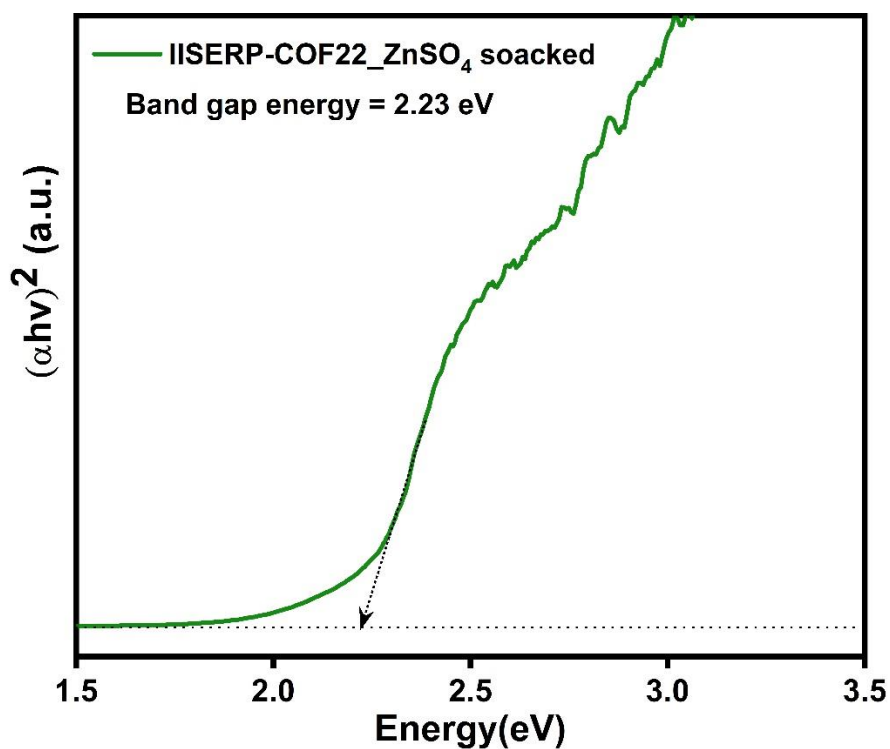


Figure A.3.32. Tauc plot to obtain the band gap of IISERP-COF22 soaked in 3M ZnSO₄ using solid-state UV-Vis spectra.

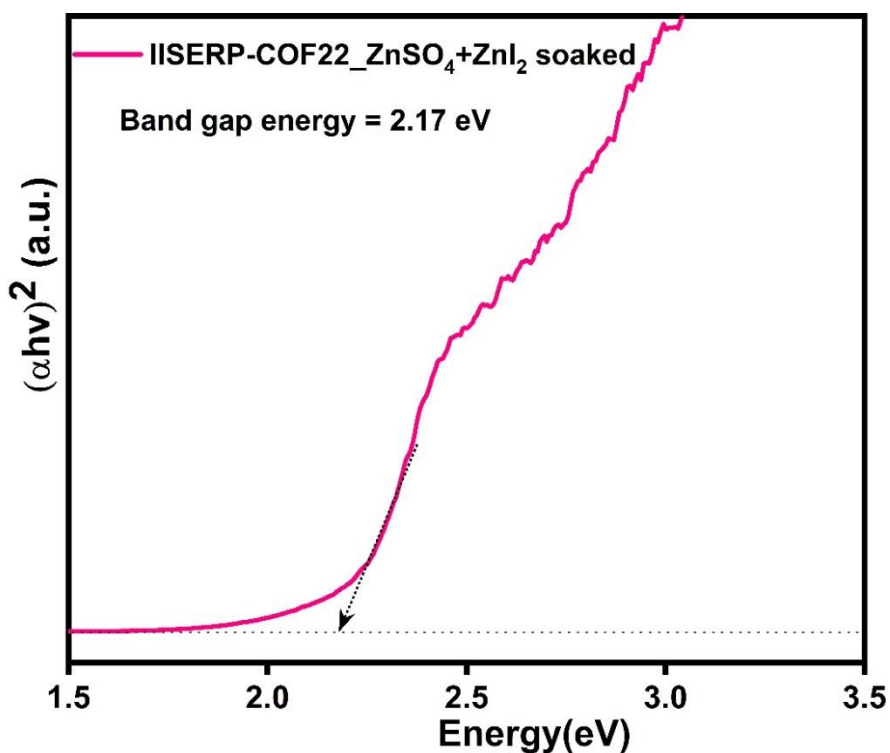


Figure A.3.33. Tauc plot to obtain the band gap of IISERP-COF22 soaked in 3M ZnSO₄+ 0.2M ZnI₂ using solid-state UV-Vis spectra.

Computational details:

For the $[\text{Zn}(\text{H}_2\text{O})_6][\text{I}_3^-]_2@\text{COF}$, the structure was modelled using the simulated annealing routine. About 8 molecules of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, 16 units of I_3^- and 14 water molecules were dispersed into a $2 \times 2 \times 2$ supercell of the COF. None of the atoms were constrained. The final structure converged well with a total energy -54908 eV/unit-cell at 0K. Formula: $\text{C}_{204}\text{H}_{34}\text{N}_{40}\text{O}_{12}$, M.wt. = 3236.77 $[\text{Zn}(\text{H}_2\text{O})_6][\text{I}_3^-]_2@\text{COF}$. The following parameters were employed for this simulated annealing (Ref CS1-CS4): The structure was optimized using the automatic temperature control about 100000 cycles/cell were used. Drieding force fields were used in conjugation with a Q_{eq} charge equilibration method. The electrostatic terms were treated with a charge group cut off of 15.5 Å, while the van der Waals was truncated using a Cubic spline method with a cut off distance of 15.5 Å and a spline width of 1 Å.

To analyze the interaction sites of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and the I_3^- and the effect of free water molecules trapped in the same space of the COF, we used molecular dynamics calculations. Forcite dynamics was used and the dynamics was evaluated at 298K. The radial distribution functions (RDFs) extracted from detailed MD simulations carried out using the Forcite Dynamics. The lowest energy configuration from the simulated annealing routine was applied as the input for the MD. A 100 ns NPT MD simulation (1.0 fs time step; $T = 298\text{K}$; $P = 1\text{bar}$) was used to reach the equilibrium state; the framework was allowed to relax, but no big change was observed in the lattice parameter of the equilibrated structure.(CS5-C7) We employed Drieding force fields. An atomic/Ewald summation method was used to handle the electrostatics and van der Waals interactions, which were optimized with a cut-off of 12.5 Å and the hydrogen bond cut off was placed at 4.5 Å. The temperature was controlled using the Nose method employing a Q ratio of 0.01, while the pressure was controlled using the Berendsen Barostat, and the initial velocities were set to be Random from a temperature-dependent Gaussian distribution.(CS8) The equilibrated structure was then optimized using a 100ns NVE ensemble available in the Forcite MD simulation (1.0 fs time step) to obtain the final configuration at the lowest energy state.(CS9) This was used to calculate the RDF. The Mean Square Displacement vs. time plots were calculated employing 1000 independent frames from the MD and linear fit was used to calculate the diffusion coefficients for each gas.(CS10)

References:

- CS1. Cerný, V. "A thermodynamical approach to the travelling salesman problem: an efficient simulation algorithm", *J. Optim. Theor. Appl.*, **45**, 41-51 (1985).
- CS2. Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd Edition, Academic Press: San Diego (2002).
- CS3. Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. "Optimization by Simulated Annealing", *Science*, **220**, no. 4598, 671-680 (1983).

- CS4. Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. "Equation of State Calculations by Fast Computing Machines", *J. Chem. Phys.*, **21**, 1087 (1953).
- CS5. NPT: Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. "Molecular dynamics with coupling to an external bath", *J. Chem. Phys.*, **81**, 3684-3690 (1984)
- CS6. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, Clarendon Press: Oxford (1987).
- CS7. Andersen, H. C. "Molecular dynamics simulations at constant pressure and/or temperature", *J. Chem. Phys.*, **72**, 2384 (1980).
- CS8. Forcite Velocity intergrater: Verlet, L. "Computer experiments on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules", *Phys. Rev.*, **159**, 98-103 (1967).
- CS9. Ray, J. R. *Comput. Phys. Rep.*, **8**, 109 (1988) and references therein.
- CS10. M. Meunier "Diffusion coefficients of small gas molecules in amorphous cis-1,4-polybutadiene estimate by molecular dynamics simulations", *J. Chem. Phys.*, **123**, 134906 (2005).

Materials and methods for CON and COF synthesis:**Synthesis of 2, 4, 6 Triformyl Phloroglucinol:**

This compound was synthesized following previously reported method[#].

[#] Chong et al. Org. Lett., Vol. 5, No. 21, 2003 and Richthofen et al. Z. Naturforsch. 2013, 68b, 64-86.

2,4,6-Trimethoxy-benzene-1,3,5-tricarbaldehyde:

This compound was synthesized following the previously reported method with slight modification #.

[#] Li et al. Org. Lett. 2005, 7, 3, 443–446 and Halder Chong et al. Angew. Chem. Int. Ed. 2018, 57, 5797.

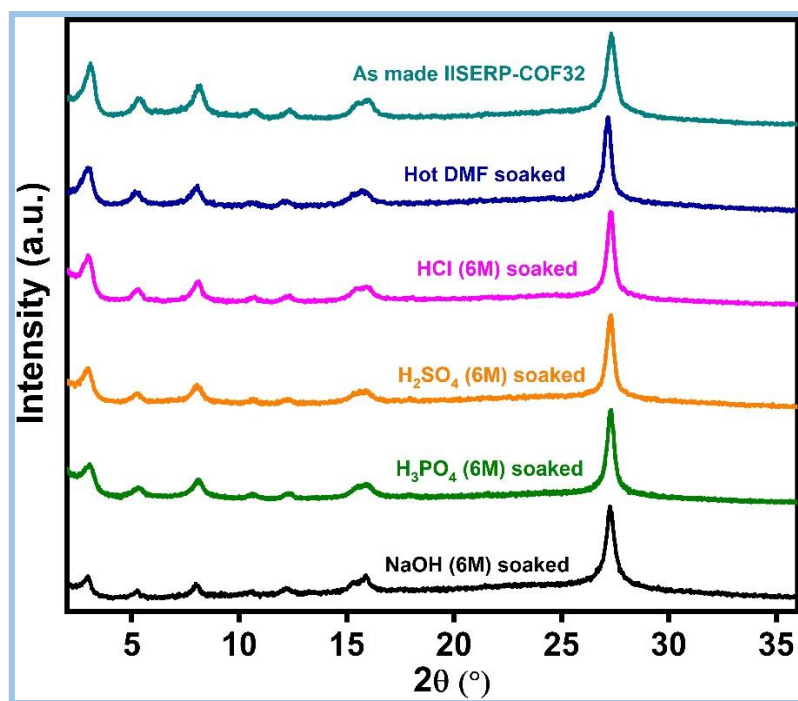


Figure A.4.1. PXRD patterns of the IISERP-COF32 soaked in different acids, bases, and solvents show the chemical stability of COF.

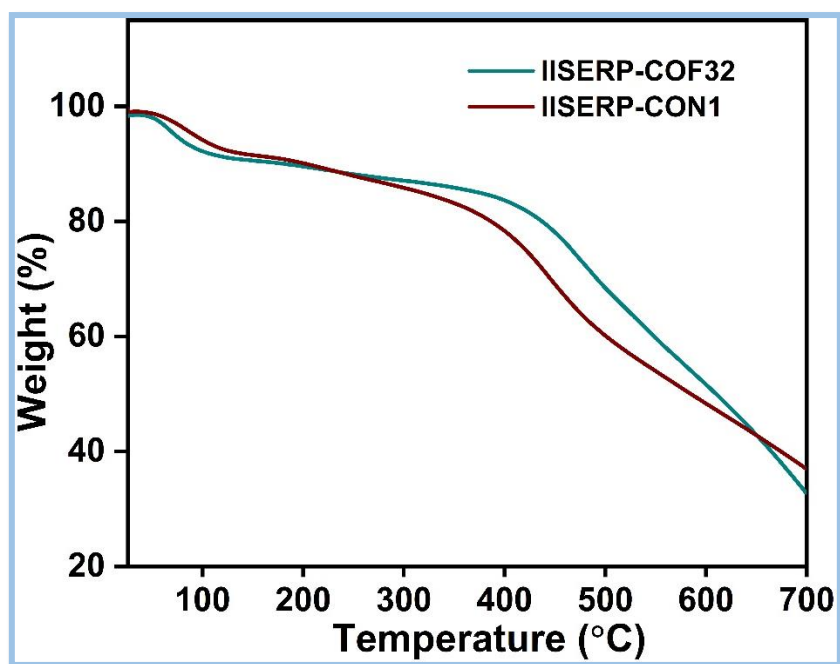


Figure A.4.2. Thermogravimetric analysis of IISERP-CON1 and IISERP-COF32 N₂ flow at 5K/min rate.

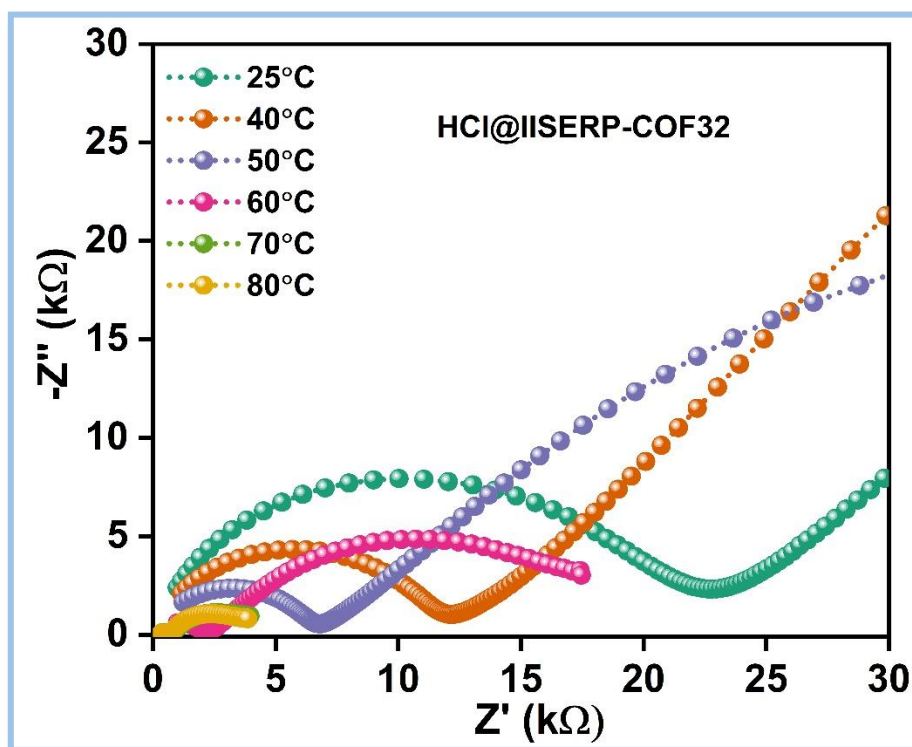


Figure A.4.3. Comparative Nyquist plots of HCl@IISERP-COF32 were measured with circular pellets under 95% RH at different temperatures.

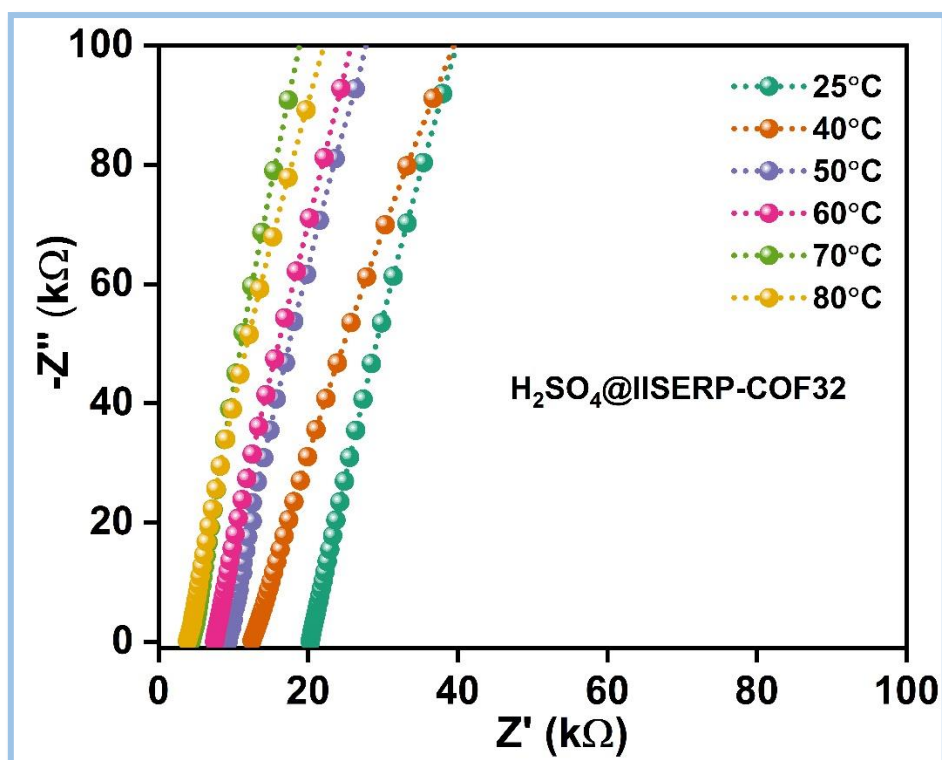


Figure A.4.4. Comparative Nyquist plots of H₂SO₄@IISERP-COF32 were measured with circular pellets under 95% RH at different temperatures.

Activation energy calculation

The activation energy was obtained using the Arrhenius equation where m is the slope of the plot between $\ln \sigma$ Vs $1000/T$ and the R is the gas constant with the value of 8.314 J/mol.

$$\sigma = A \exp(-E_a/RT)$$

$$\ln \sigma = (-E_a/RT) + \ln A$$

$$y = mx + C$$

$$-m = -\text{slop} = E_a/R$$

$$E_a = -m \times R$$

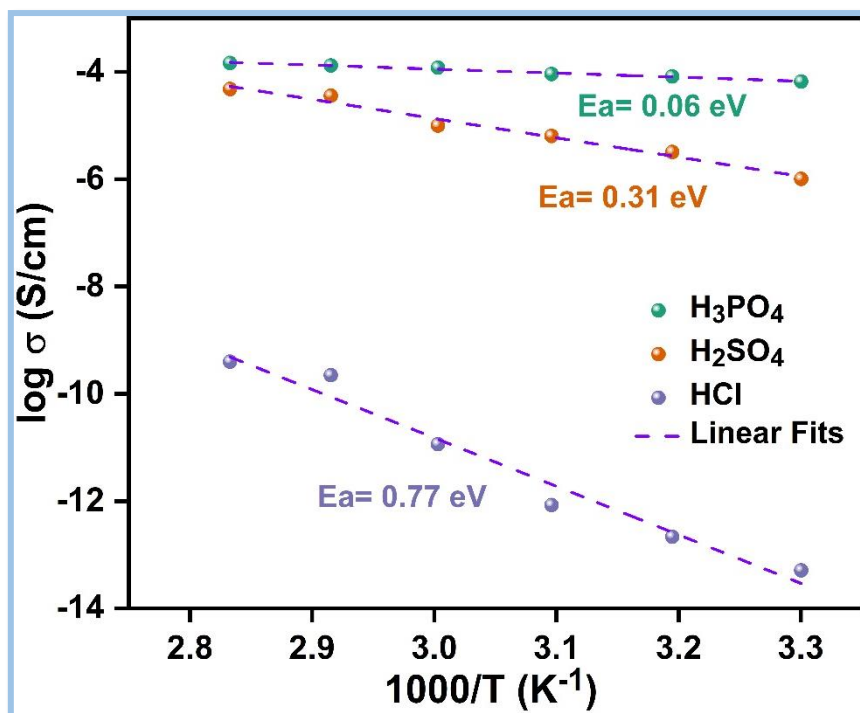


Figure A.4.5. Comparative Arrhenius plots of IISERP-COF32 loaded with different acids for activation energies.

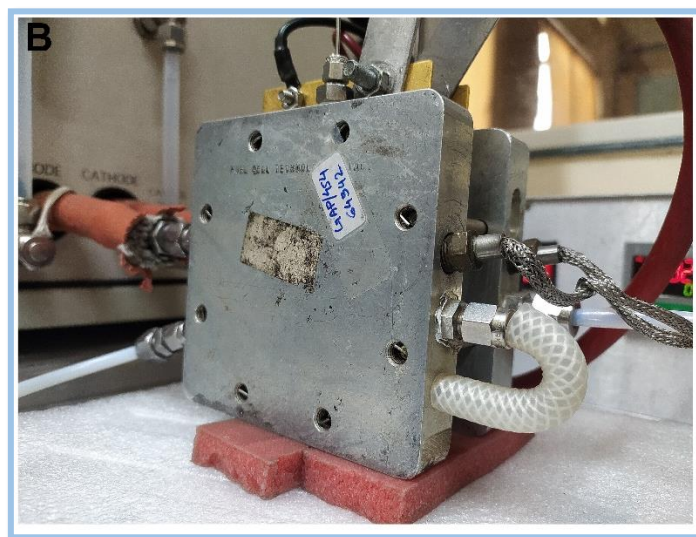


Figure A.4.6 (A) A digital photograph of a 2x2 single cell assembly of fuel cell fixture.

First author (*Included in thesis*)

- 1) **Kushwaha, R.**; Jain, C.; Shekhar, P.; Vinod, C. P.; Vaidhyanathan, R., Made to Measure Squaramide COF Cathode for Zn Dual-Ion Battery with Enriched Storage via Redox Electrolyte. (*Adv. Energy Mater.* **2023**, *13*, 2301049)
- 2) **Kushwaha, R.**; Rase, D.; Jain, C.; Vaidhyanathan, R., Transformation of Covalent Organic Nanosheet to Covalent Organic Framework via Molecular Level Engineering to Achieve High-Performance Proton Conduction for Fuel Cell Application. (*Manuscript Under preparation*)
- 3) **Kushwaha, R.**; Haldar, S.; Shekhar, P.; Krishnan, A.; Saha, J.; Hui, P.; Vinod, C. P.; Subramaniam, C.; Vaidhyanathan, R., Exceptional Capacitance Enhancement of a Non-Conducting COF through Potential-Driven Chemical Modulation by Redox Electrolyte. *Adv. Energy Mater.* **2021**, *11*, 2003626.

First author (*Not included in thesis*)

- 4) **Kushwaha, R.**; Jain, C.; Shekhar, P.; Vinod, C. P.; Vaidhyanathan, R., Capacity Amplification of Triazine-based Covalent Organic Framework via Multicomponent Reaction Thiazole-Linked for Li-ion battery. (*Manuscript Under preparation*)
- 5) Devulapalli, V.S.D.¹; **Kushwaha, R.**¹; Ovalle, E.; Singh, H.D.; Shekhar, P.; Chakraborty, D.; Vinod, C.P.; Vaidhyanathan, R.; Borguet, E., Synergistic Electronic Effects in AuCo Nanoparticles Stabilized in a Triazine-Based Covalent Organic Framework: A Catalyst for Methyl Orange and Methylene Blue Reduction *ACS Appl. Nano Mater.* **2022**, *5*, 4744–4753. (**¹co-first authors**)
- 6) **Kushwaha, R.**; Kaleeswaran, D.; Haldar, S.; Chakraborty, D.; Mullangi, D.; Borah, A.; Vinod, C. P.; Murugavel, R.; Vaidhyanathan, R., Nanoporous Covalent Organic Framework Embedded with Fe/Fe₃O₄ Nanoparticles as Air-Stable Low-Density Nanomagnets. *ACS Appl. Nano Mater.* **2020**, *3*, 9088–9096.
- 7) Haldar, S.¹; **Kushwaha, R.**¹, Maity, R.; Vaidhyanathan, R., Pyridine-Rich Covalent Organic Frameworks as High-Performance Solid-State Supercapacitors. *ACS Materials Lett.* **2019**, *1*, 490–497. (**¹co-first authors**)

Co-authors:

- 8) Jain, C.; **Kushwaha, R.**; Rase, D.; Shekhar, P.; Shelke, A.; Sonwani, D.; Ajithkumar, T. G.; Vinod, C. P.; Vaidhyanathan R. Tailoring COFs: Transforming Nonconducting 2D Layered COF into a Conducting Quasi-3D Architecture via Interlayer Knitting with Polypyrrole. *J. Am. Chem. Soc.* **2024**, *146*, 1, 487–499 (Just accepted)
- 9) Nandi, S.; Singh, H. D.; Shekhar, P.; Chakraborty, D.; **Kushwaha, R.**; Vaidhyanathan, R. An intrinsically zwitter-ionic COF: a carboxylic acid and pseudo-tetrahedral sp³ nitrogen functionalized covalent organic framework with potential for humidity sensing. *J. Mater. Chem. A*, **2024**, *12*, 2839-2847. (Just accepted)
- 10) Chakraborty, D.; Nandi, S.; **Kushwaha, R.**; Kaleeswaran, D.; Vaidhyanathan, R., Viologen functionalized C–C bonded cationic polymers for oxo-anion pollutant removal from aqueous medium. *Materials Research Bulletin*, **2022**, *146*, 111614.
- 11) Halder, S.; Roy, K.; **Kushwaha, R.**; Ogale, S.; Vaidhyanathan, R., Chemical Exfoliation as a Controlled Route to Enhance the Anodic Performance of COF in LIB. *Adv. Energy Mater.*, **2019**, *9*, 1902428.
- 12) Chakraborty, D.; Shekhar, P.; Singh, H. D.; **Kushwaha, R.**; Vinod, C. P.; Vaidhyanathan, R., Ag Nanoparticles Supported on a Resorcinol-Phenylenediamine-Based Covalent Organic Framework for Chemical Fixation of CO₂. *Chem. Asian J.*, **2019**, *14*, 4767–4773.
- 13) Chakraborty, D.; Nandi, S.; Sinnwell, M. A.; Liu, J.; **Kushwaha, R.**; Thallapally, P. K.; Vaidhyanathan, R., Hyper-Cross-linked Porous Organic Frameworks with Ultramicropores for Selective Xenon Capture. *ACS Appl. Mater. Interfaces*, **2019**, *11*, 13279–13284.
- 14) Halder, S.; Chakraborty, D.; Roy, B.; Banappanavar, G.; **Kushwaha, R.**; Mullangi, D.; Hazra, P.; Kabra, D.; Vaidhyanathan, R., Anthracene-Resorcinol Derived Covalent Organic Framework as Flexible White Light Emitter. *J. Am. Chem. Soc.*, **2018**, *140*, 13367–13374.
- 15) Maity, R.; Chakraborty, D.; Nandi, S.; **Kushwaha, R.**; Vaidhyanathan, R., Microporous mixed-metal mixed-ligand metal organic framework for selective CO₂ capture. *Cryst. Eng. Comm.*, **2018**, *20*, 6088–6093.

Patents:

- 1) **Kushwaha, R.**; Vaidhyanathan, R. “Method Of Enhancing The Supercapacitance Of Covalent Organic Framework Via Use Of Redox Active Additives In Electrolyte”. Applied for [Indian Patent 202021021759](#).
- 2) **Kushwaha, R.**; Vaidhyanathan, R. “Covalent Organic Framework Derived Lightweight Nanomagnets and a chemical method thereof”. Applied for [Indian Patent 202021004764](#).