# Abstract

MOFs are a novel class of hybrid materials with intriguing characteristics like ultra-high surface area, controllable nanopores, regular crystalline structure, high thermal stability, etc. They are composed of metal nodes connected to organic linkers through coordination bonding. Prof. Yaghi initiated the field of MOF research in the late 1990s and presented a framework consisting of organic molecules and metal centers that binds together to create a 1D, 2D, or 3D network. The basic repeating unit of MOF is the primary building unit (PBU) which is composed of metal node and it forms coordination bond with the organic linker. When several PBUs connect together to produce a specific pattern, it gives rise to the secondary building unit (SBU). This SBU serves as the foundation for the structure of the MOF because each SBU possesses a unique intrinsic geometry that determines the topology of the MOF. The structural, optical, morphological, and other properties of MOF vary depending on the topology. With the passing of decades, an enormous number of MOFs have been invented, providing new avenues in the fields of gas separation, absorption, sequestration, catalysis, and sensing. The redox active sites present in the MOF drives its application towards the catalytic activities. In spite of being multifunctional with versatility, MOF is less utilized in the fields of energy storage and optoelectronics as it is electrically insulating by nature because of a lack of free charge carriers and restricted charge transport pathways. Owing to its highly porous nature, it offers a suitable platform for guest accommodation in their specific nanochannels, where guest molecules show unique properties regarding their motion, charge transfer, electronic properties, magnetic properties, phase transition, etc. One of the strategies to reduce the energy barriers for charge transfer and achieve conductivity in MOFs is the encapsulation of guests within the pores of MOFs. Via guest-guest or guest-framework interaction, electroactive species like metal nanoparticles, metal oxides, conducting polymers, and organic molecules can assist the MOF in conducting electricity by using a through-space, through-bond, or hopping conduction mechanism. A recent trend aimed at improving MOF's physical-chemical characteristics involves introducing a controlled amount of structural defects. Defects such as missing linkers, nodes, modified linkers, modified nodes, etc. are the primary types of defects observed in MOFs. There are two ways to intentionally incorporate defects into MOF: either during synthesis or post synthetic treatment. A defective MOF is produced when large amount of modulator is used to slow down the crystallization process during synthesis. Usually, mechanical treatment, severe activation conditions, acid/base

treatment, etc., are used to create post-synthetic defects. Ion beam irradiation is a noteworthy technique to modify the structural, chemical, electrical and electrochemical properties of MOF by controlled application of a selected ion energy and fluence. The bombardment of high-energy ions in the target atoms modifies the materials through different processes. Two distinct processes are (i) loss of nuclear energy through elastic collisions with nuclei; and (ii) loss of electronic energy through inelastic collisions with the target material's atomic electrons. In swift heavy ion (SHI) irradiation, the electronic energy loss processes dominate, which contribute to the electronic defects, excitation, or ionisation of atomic electrons.

The electrically conducting MOF with the advantage of high surface area and adjustable pore structure is a promising candidate for electrode material in electrochemical sensing applications. A high sensitivity, stability and specific selectivity towards analytes are the basic requirements of an electrochemical sensor. Electrochemical sensing works on the principle of analyte-electrode interaction and converting it into a quantifiable signal. The detection of environmental contaminates found in terrestrial and aquatic space are need to be monitored because of non-biodegradability and toxicity. Such inorganic pollutants are heavy metal like Cd, Pb, Hg etc. and organic pollutant like benzo-pyrene, naphthalene, dihyroxybenzene isomers etc. These pollutants have a tendency to bind covalently with organic substances and may be considered hazardous if their concentration in the air, water, or soil exceeds a predetermined threshold. In addition to detecting pollutants in the surroundings, MOFs can be investigated for the biosensing of various proteins, antibodies, enzymes, oligonucleotides, etc. Because MOFs have a substantial surface area with tunable binding sites, they provide a large interface for biomolecule immobilization.

The modified MOFs with guest insertion and defect creation via SHI irradiation can be applied in electrochemical and biosensing applications. The modifications in the MOFs can improve selectivity by introducing new active sites for the adsorption of particular targets and can contribute to better sensitivity through an increase in electrical conductivity.

According to the framed objectives, the thesis has been organized in eight chapters as discussed follows:

**Chapter 1:**

The first chapter introduces the host material metal organic framework (MOF) used during for the thesis work and its applications in various field. This chapter also includes the different strategies for enhancing the property of the material for using it as an electrode material in electrochemical application. These strategies comprise adding different types of guest materials into the framework and adding modification in the structure with swift heavy ion irradiation. Brief description of electrochemical sensors, working principles, types of electrochemical sensors has also been described in this chapter. Lastly the objective and thesis structure has been discussed.

**Chapter 2:**

This chapter highlights the properties of materials used for synthesis of Zr-based MOF UiO-66, guest molecules metal oxide nanoparticles ($Ag_2O$) and conducting polymer Poly(3,4-ethylenedioxythiophene) (PEDOT). Description of all the analytes used for electrochemical sensing are also been discussed in this chapter. The various synthetic routes adopted for the synthesis of UiO-66, $Ag_2O$ incorporated UiO-66 and PEDOT inserted UiO-66 has been discussed. UiO-66 was prepared by using a solvothermal route and post-synthetically modified by loading $Ag_2O$ where $AgNO_3$ was reduced with chemical agents in one sample and with natural agent in another sample, the samples were named as S1(MOF) and S2(MOF). PEDOT was inserted by in-situ polymerization of monomers by adding oxidizing agent $FeCl_3$, sample obtained was named as PEDOT@UiO-66. The fabrication of prepared materials into ITO working electrodes through drop casting and slurry coating has also been discussed in this chapter. Lastly the basic principles of various characterization techniques like XRD, FTIR, TEM, SEM, CV, DPV etc. employed for material property investigation has been presented in the chapter.

**Chapter 3:**

In this chapter, the first section talks about the structural and morphological properties of UiO-66 after incorporation of $Ag_2O$ into the framework through different synthesis approaches. Here, XRD and FTIR confirmed the loading of $Ag_2O$ into UiO-66 without affecting its structure. The FESEM images reveals the location of $Ag_2O$ NPs in the framework structure in two different approaches. BET analysis discusses the alteration in the porous structure and specific surface area of UiO-66 as result of $Ag_2O$ loading.

The second section presents the structural and morphological investigation of PEDOT inserted UiO-66. Here, XRD confirms the PEDOT insertion in the framework by keeping the structure of UiO-66 intact as the characteristic peaks of XRD are unaltered. TEM imaging and EDX confirms the presence of PEDOT in the structure. From BET and Pore size distribution analysis, the partial fulfillment of pores by PEDOT has been confirmed. Raman spectroscopy analysis revealed the alteration in the conformation of the PEDOT upon confining it into the pores.

**Chapter 4:**

After introducing the guest material into the UiO-66 framework, it's affect on the electrical properties has been discussed in this chapter. The first part discusses the enhancement in the electrical property after loading $Ag_2O$ in UiO-66 through two different approaches. The conductivity of $Ag_2O$ incorporated UiO-66 has significantly increased from its pristine state. S1(MOF) has a partially rectifying nature of I-V plot with predominant linearity further which reveals the presence of space charge limited current (SCLC) transport mechanism followed by Ohmic mechanism. Similarly, S2(MOF) also exhibits a rectifying nature of I-V plot which is also governed by Ohmic and SCLC transport mechanism where current linearly increases with voltage. The temperature dependent conductivity of these two materials shows the absence of thermionic emission of charge carriers which usually takes place in semiconducting materials. In these materials, the conductivity rather decreased with increasing temperature.

The second part discusses the electrical behavior of PEDOT inserted UiO-66 which shows an enhancement in the conductivity after PEDOT polymerization inside the pores. The transport property analysis reveals the thermionic emission mechanism of charge carriers. This finding was further supported by the temperature dependent conductivity studies. The material showed a hopping transport mechanism as well.

**Chapter 5:**

Herein, electrochemical sensing strategy for detecting heavy metal ions present in aqueous media using $Ag_2O$ NP incorporated metal organic framework (MOF) UiO-66 electrodes has discussed. In these conducting UiO-66, the NPs were believed to act as the electric current enhancer while UiO-66 provided adsorption sites for heavy metal ions. The ITO electrodes surface was fabricated with as prepared $Ag_2O$ loaded UiO-66 namely S1(MOF) and S2(MOF) for the electrochemical detection of $Hg^{2+}$ and $Cd^{2+}$ independently as well as simultaneously. The detection of heavy metals was performed by the modified electrodes through differential pulse stripping voltammetry (DPSV) which offered excellent selectivity and with sensitivity values up to 551 $\mu A \mu M^{-1} cm^{-2}$ for $Cd^{2+}$ and 341.2 $\mu A \mu M^{-1} cm^{-2}$ for $Hg^{2+}$. The limit of detection (LOD) for the respective cases, were estimated to be 0.008 μM and 0.003 μM. The material under investigation exhibits exceptional qualities, showcasing remarkable reproducibility, repeatability, stability, and selectivity. The material has also been verified with real water samples with good recoveries.

**Chapter 6:**

This chapter discusses the application of PEDOT polymerised UiO-66 in individual and simultaneous sensing of hydroquinone and catechol. Since the PEDOT inserted UiO-66 showed enhanced electrical property by retaining its porous structure, the material was used in modifying ITO glass surface to apply in an electrochemical sensing application. PEDOT@UiO-66 proved to be a suitable electrocatalyst for simultaneous redox reaction with hydroxybenzene isomers hydroquinone (HQ) and catechol (CT). The modified electrode with PEDOT@UiO-66 could able to determine the analytes in a linear range of 10 μM – 300 μM with a lower limit of detection for both CT and HQ. One of the significant achievements of the material is its high sensitivity for HQ and CT. The outcomes of the experiment demonstrated that the modified electrode was simply constructed under control and shown exceptional stability. In terms of repeatability and reproducibility, the electrode performance was satisfactory. The electrodes were also used for real sample analysis in lake water and good recovery of 90-95 % has been observed.

**Chapter 7**

This chapter discusses the SHI irradiation effect on structure, morphology, electrical and electrochemical behaviour of UiO-66 and its application in detecting antigen goat anti mouse IgG after converting it into immunosensor. Defects have been incorporated to the crystal structure of UiO-66 films by swift heavy ion (SHI) irradiation employing a 60 MeV $N^{5+}$ ion beam with fluences 5 $x10^{10}$ ions/$cm^2$, 5 $x10^{11}$ ions/$cm^2$ and 1 $x10^{12}$ ions/$cm^2$. The XRD analysis revealed the impact of fluence in the structure of UiO-66 where the first two fluences have kept structural integrity but fluence 1 $x10^{12}$ ions/$cm^2$ has degraded the structure. From the FTIR and Raman spectra analysis, the presence of missing linker defects was realised. Further electrical and electrochemical behaviour of irradiated films were compared with the pristine UiO-66 by current-voltage (I-V) and cyclic voltammetry (CV) measurements. The structural analysis suggested that there may have been missing linker defects in the structure following radiation, which would have increased the films conductivity. The fluence of 5 $x10^{11}$ ions/$cm^2$ showed the superior conductivity than the pristine and the UiO-66 irradiated with fluence 1 $x10^{12}$ ions/$cm^2$. Later the UiO-66 films were converted into biosensing electrodes for the detection of antigen goat anti mouse IgG. In the biosensing electrodes, UiO-66 played the role of transducer element which signifies the biorecognition process and immobilised mouse IgG behaves as the bioreceptor. Differential pulse voltammetry (DPV) technique was used to quantify the detection process of antigen. As expected, the electrode irradiated with fluence 5 $x10^{11}$ ions/$cm^2$ have a greater efficiency in detecting the analyte with lower LOD in a wide linear-range with a good sensitivity.

**Chapter 8**

It addresses the conclusion remarks of all the chapters and future scope of the work.

**Keywords:** Metal organic framework, Conducting polymer, Conductivity, Cyclic voltammetry, Electrochemical sensing, Biosensing, SHI irradiation.